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Microwave treatment of hazardous wastes : chemical fixation of insoluble non-volatile, chemically non-reactive organics in soil

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ABSTRACT

Title of Thesis: Microwave Treatment of Hazardous Wastes:
 "Chemical Fixation" of Insoluble, Non-Volatile
 Chemically Non-Reactive Organics in Soil

Naihong Zhu: Master of Science, 1991

Thesis Directed By: Leonard Dauerman, Associate Professor of Chemical
 Engineering, Chemistry and Environmental Science

Microwave treatment of hazardous wastes like dioxin-contaminated soil potentially fills a great need for a remediation technology which potentially can be applied in-situ: the EPA has concluded from a risk assessment study that it is the excavation and transportation of such wastes that poses the greatest risk. Studies have been carried out on a surrogate for dioxin, namely, 9,10-anthraquinone because it has similar chemical and physical properties but it is not toxic. It was found in microwave treatment studies that, at temperatures attainable in-situ, anthraquinone became non-extractable. A model was proposed which postulated that as water was removed from soil aggregates, anthraquinone adsorbed directly on the humus and clay fractions, and then reacted chemically. This led to spectroscopic studies to determine directly whether or not anthraquinone did undergo a chemical reaction. Those studies were carried out using DRIFT (diffuse reflectance Fourier transform spectroscopy) and ATR/FTIR (horizontal attenuated total reflectance Fourier transform spectroscopy). Bands shifts and formation suggestive of possible chemical reactions were found after microwave treatment of anthraquinone adsorbed on humus and kaolin clay, respectively.

**MICROWAVE TREATMENT OF HAZARDOUS WASTES:
"CHEMICAL FIXATION" OF INSOLUBLE, NON-VOLATILE,
CHEMICALLY NON-REACTIVE ORGANICS IN SOIL**

by

NAIHONG ZHU

**Thesis Submitted to the Graduate Division of
New Jersey Institute of Technology
for
the Degree of Master of Science**

April, 1991

APPROVAL SHEET

Title of Thesis: Microwave Treatment of Hazardous Wastes: "Chemical
Fixation" of Insoluble, Non-Volatile Chemically Non-Reactive
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CHAPTER 1. INTRODUCTION

1.1 BACKGROUND

Microwave treatment is one of the few technologies potentially capable of remediating soil contaminated with hazardous materials in-situ. Bench-scale studies and pilot plant studies on the applications of microwave energy for the treatment of hazardous wastes have been carried out in this laboratory (The Microwave Treatment of Hazardous Wastes Laboratory of The Northeast Hazardous Substance Management Research Center) for the past five years.

The studies in this laboratory include the following:

- (1) The investigation of the decontamination of volatile or semi-volatile organic-contaminated soil (Windgasse 1988; Fan 1989; He 1990).

The purpose of the study of the remediation of soil contaminated with volatile and semi-volatile organics was to develop a process to effect steam distillation of the organics by heating with microwave energy. Steam distillation, a mass transfer process in which organic contaminants are physically vaporized and recovered, is carried out at a relatively low temperature so that there will be no change in the chemical state of the soil and the volatiles or semi-volatiles, respectively. This means that a new waste stream is not created after microwave treatment. This process can be effected practically only by microwave because thermal methods such as incineration establish diffusion gradients through the soil causing the water to diffuse into the heated air stream rather than boil with the organics in-situ. Using thermal heating, the water will not vaporize in conjunction with the organic

contaminants; therefore, unlike steam distillation, the sum of the respective vapor pressures will not reach the ambient pressure.

(2) The investigation of the applicability of microwave technology to the remediation of soil contaminated with heavy metals (Jou 1989; Ibrahim 1990; He 1990).

This investigation was carried out on a hexavalent chromium-contaminated soil system. The studies showed that hexavalent chromium was converted to a trivalent state in the crystalline forms of chromite (FeCr_2O_4) and Cr_2O_3 after microwave energy treatment. The trivalent chromium-contaminated soil is non-hazardous [under regulations adopted to implement the United States Resource Recovery and Conservation Act (RCRA)].

(3) The investigation of the regeneration of spent granulated activated charcoal (GAC) (Mahesh 1989).

The regeneration of GAC saturated with a non-volatile organic methylene blue had been investigated. From the studies, it was inferred that the following mechanism was involved when methylene blue-saturated GAC was heated by microwave energy: water which was adsorbed in the GAC pores vaporized forcing out the air and formed an anaerobic atmosphere; methylene blue was pyrolyzed when the system was heated up above the decomposition temperature of methylene blue; and the pyrolyzed methylene blue was fused to and became part of the GAC.

(4) The investigation of the destruction of hazardous material in the gas phase (Windgasse 1988).

The destruction of hazardous substance in the gas phase upon contact with "lossy" materials, which are strong microwave absorbers like silicon carbide, either in fluidized beds or packed beds had been investigated. It was found that volatilized trichloroethylene could be destroyed up to 100% passing through a fixed-bed flow reactor or fluidized bed reactor.

(5) The investigation of decontamination of non-volatile organic-contaminated soil (Gu 1990).

The applicability of microwave technology to the remediation of soil contaminated with an insoluble, non-volatile, relatively non-chemically reactive organic compound had been investigated. The results from the study of saturated GAC with a non-volatile organic suggested that a potentially significant application of microwave technology to the remediation of soil contaminated with non-volatile organics, that is, the behavior of the soil as a substrate might be analogous to that of GAC as a substrate. Bench-scale experiments were carried out on non-volatile organic-contaminated soil system using microwave energy at a relatively low temperature. The following model has been developed, as a result of these studies:

(a) spilled organics are adsorbed in multilayers on soil particles which are bound together by water;

(b) microwave treatment vaporizes the water and causes the diffusion of the non-volatile organics leading to monolayer adsorption of the organics on the soil;

(c) the soil heats up further to approximately 200 °C, a temperature attainable by in-situ microwave treatment, causing reactions between the indigenous organics and inorganics in the soil and the monolayer adsorbed spilled organic;

(d) the reacted spilled organic is "chemical fixed" and is no longer extractable.

The chemical fixation is inferred from the experimental data.

Summarizing, the investigations in this laboratory offer strong evidence that microwave technology is potentially a useful, powerful, and cost-effective method to effect the remediation of hazardous wastes in the following ways: steam distillation of volatiles and semi-volatiles; immobilization of heavy metals; destruction of the volatilized organics with beds of "lossy" solids; and "fixation" of non-volatile organic chemicals.

1.2 OBJECTIVE

The objective of this study was to further investigate the application of microwave technology to the remediation of non-volatile organic-impregnated soil: the development of a method to obtain spectroscopic evidence for organic reactions with soil. The previous study in this laboratory indicated that insoluble, non-volatile organic chemicals might be fixed when a non-volatile organic-contaminated soil system was treated by microwave energy. But the "chemical fixation" was only a postulate; in the previous study no direct evidence was obtained for this reaction.

To obtain direct evidence, in this thesis the applicability of the following analytical techniques were investigated: Fourier transform infrared spectroscopy (FTIR), GC/FTIR, GC/MS, attenuated total reflectance FTIR (ATR/FTIR), diffuse reflectance Fourier transform infrared spectroscopy (DRIFT), and UV-Visible spectroscopy, respectively.

1.3 Scope of the Investigation

The following activities were carried out as part of this study:

- (1) Literature reviews on the following topics: the effects of microwave heating of materials; the application of infrared techniques, especially Fourier Transform Infrared Spectroscopy (FTIR) and diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) on the interactions of organics and soil (humic substances, clay, and minerals); the physical and chemical properties of 9,10-anthraquinone which was chosen as the surrogate for dioxin.
- (2) Microwave energy treatments of anthraquinone-impregnated sandy soil, and clay soil, respectively.
- (3) Comparison of the extractability of anthraquinone-impregnated soil by two extraction methods: Soxhlet and Ultrasonic extraction. Also, the measurement of the moisture levels of soils.
- (4) Using GC/MS, FTIR, GC/FTIR, and UV-VIS spectroscopy to detect anthraquinone or any organics in extracts from the samples of anthraquinone-impregnated soils or clay before and after microwave energy treatment.

(5) Using DRIFT and ATR/FTIR to collect spectra of the mixtures of anthraquinone-clay and anthraquinone-humus (solid sample) before and after microwave treatment.

The review of the literature is presented in Chapter 2; the microwave treatment studies (2 above), in Chapter 3 and Chapter 6; the extraction and moisture measurement studies (3 above), in Chapter 4 and Chapter 5; the measurements of FTIR and GC/FTIR (4 above), in Chapter 7 and Chapter 10; the measurements of DRIFT and ATR/FTIR (5 above), in Chapter 8 and Chapter 9. While the results of the experimental work are discussed in each chapter in which such results are presented, the overall conclusions and future research needs are presented in Chapter 11. Instrumental operating parameters are presented in Appendix I. Raw data from the experiments are listed in Appendix II. The publications of the Microwave Treatment of Hazardous Waste Laboratory of the Northeast Hazardous Substance Management Research Center are listed in Appendix III. The list of references is given at the end of the thesis.

CHAPTER 2. REVIEW OF THE LITERATURE

2.1 PREVIOUS RESEARCH

2.1.1 Previous Research On Microwave Technology For Remediation Of Hazardous Solid Wastes

Until recently, there had been little research into microwave treatment of soils contaminated with hazardous wastes. Microwave technology on the remediation of contaminated substrates is in an embryonic stage (Fitzpatrick 1987; Hertzler 1979; Oda 1990; Suzuki 1990; Varma 1990; Weston 1989). In 1987, our lab began to investigate the possibility and capability of applying microwave technology to effect the remediation of soil contaminated by hazardous waste.

Emerging technologies utilize electromagnetic radiation in different ways. For example, Illinois Institute of Technology reported on an in-situ radio-frequency process (IRF). It is now being developed with Roy F. Weston, Inc. (Weston 1989). This process, originally developed to extract shale oil (that's why the RF frequency and not the microwave frequency was used), was applied to soil remediation. Tubular electrodes were inserted into contaminated soil, and were then oscillated with radio-frequency energy; the soil was heated to a temperature up to 600°C, for fourteen (14) days, vaporizing the toxic contaminants. Their approach differs from ours in several major ways:

- (1) Our approach is to remove volatiles by steam distillation; theirs, to heat the soil up to 600°C. Microwave frequencies are optimum for the water absorption; RF,

shale. (It is the fact that water is a poor absorber of RF that it makes possible for nuclear submarines at the bottom of the ocean to stay in communication by sending RF signals thousands of miles away to a field of antennas in Michigan).

(2) Our approach is to "fix" the non-volatiles; they don't address this problem thereby limiting the application of their process to the remediation for oil spills.

(3) Likewise, they don't address the possibility that the soil is contaminated with heavy metals.

2.1.2 Previous Studies On The Sorption Interactions Between Organic Compounds And Solid Substrates

There are several techniques which are used to determine the sorptive interactions between organic compounds and solid substrates. Of the methods available to study sorption interactions between organics and soils, infrared spectroscopic methods have the potential to rapidly determine the origins and functional groups responsible for the sorptive interactions. This technique often has been used to establish the mechanisms of interaction between chromatographic substrates and organic compounds (Basila et al. 1964; Bernstein et al. 1982; Morrow and Cody 1976). The petroleum refining industry has used infrared spectroscopy to study soil structure and sorptive relationships between pesticides and soil components (White 1971; Farmer and Russell 1964; Shoval and Yariv 1979; Saltzman and Yariv 1975). Many researchers have investigated interactions between clays and organic compound types (Mohamed 1978; Mortland 1986) and interactions between toxic organic chemicals and humic substances or minerals (Gerstl et al. 1989; Stevenson 1972). In addition,

much infrared research has been done to describe the mechanisms of these interactions (Saltzman and Yariv 1975; Yariv 1966; Mortland 1976; Huang 1977).

The importance of clay-contaminant interactions has been well documented (Mortland 1986; Warren 1986). Mechanisms including ion exchange, protonation, hydrogen bonding, coordination, and catalytic degradation may be involved in the interaction between clays and organics. The use of infrared spectroscopy to study such clay/organic relationships has been described (Farmer and Russell 1964).

Fourier Transform Infrared (FTIR) spectroscopy is a method of infrared analysis which is much more sensitive than dispersive IR analysis. Through the use of FTIR spectroscopy, the mechanism of an organo-mineral sorption interaction can be determined by an analysis of the direction and magnitude of band shifts and intensity variations when the spectrum of the organic compound is compared against that of the organo-mineral complex (Fusl et al. 1983; Issacson and Saxhney, 1982; Bowen et al. 1988)

The recent development of solid state sampling / analytic techniques such as diffuse reflectance fourier transform infrared spectroscopy (DRIFT) has provided a useful, and powerful method to study organic-clay interactions (Bowen et al. 1989). Porro and Pattacini (1990) reported that DRIFT can be used for quantitative analysis of a number of silanized kaolin clays.

So far, most studies have been focused on polar organic-clay systems; there is little information to be found for the sorption interactions between non polar

organic and solid substrates and, also, interactions in organic-solid substrates because of microwave treatment.

In this study, DRIFT, ATR/FTIR, GC/MS, and several other techniques were used to develop a method to study sorption interactions between non polar organic and solid substrate because of microwave treatment.

2.2 THE BASIC PRINCIPLES OF MICROWAVE TREATMENT

In the electromagnetic radiation spectrum, the frequency range extending from 300 MHz (1 meter wavelength) to 300 GHz (1 millimeter wavelength) is generally known as microwaves. A microwave photon has an energy located in the range between roughly 1.2×10^{-6} and 1.2×10^{-3} eV.

Microwaves are mostly encountered in three kinds of applications as follows:

- (a) radar, used for detection and measurements;
- (b) radiocommunications, for point-to-point links, most particularly for satellite and space communications;
- (c) heating, drying, cooking of many different types of materials.

The study of the applicability of microwave technology to the remediation of hazardous wastes is a relatively new field of research. For this research, the principles of microwave heating are of interest in providing guidelines for the research studies.

principles of microwave heating are of interest in providing guidelines for the research studies.

Microwave radiation is composed of an electric field and a magnetic field at right angles to each other. The fundamental laws which describe the behavior of electromagnetic radiation are Maxwell's equations. Maxwell's equations, in term of phasor-vectors, are given by (Frede 1984)

$$\nabla \times \underline{E} = -j\omega \underline{B} = -j\omega \underline{\mu} \underline{H} \quad \text{V/m}^2$$

$$\nabla \times \underline{H} = \underline{J} + j\omega \underline{D} = (\sigma + j\omega \underline{\epsilon}) \underline{E} \quad \text{A/m}^2$$

$$\nabla \cdot \underline{E} = \underline{\rho} / \underline{\epsilon} \quad \text{V/m}^2$$

$$\nabla \cdot \underline{H} = 0 \quad \text{A/m}^2$$

with

\underline{E} electric phasor-vector

\underline{H} magnetic phasor-vector

\underline{B} induction phasor-vector

\underline{D} displacement phasor-vector

\underline{J} current density phasor-vector

$\underline{\rho}$ charge-density phasor

σ conductivity

$$\underline{\epsilon} = \epsilon_0 \underline{\epsilon}_r = \epsilon' - j\epsilon'' = \epsilon_0(\epsilon'_r - j\epsilon''_r) = \epsilon'(1 - j \tan \delta)$$

complex permittivity

$$\underline{\mu} = \mu_0 \underline{\mu}_r = \mu' - j\mu'' = \mu_0(\mu'_r - j\mu''_r)$$

complex permeability

The terms ϵ_r and μ_r are respectively the relative permittivity and permeability of the medium. The loss tangent $\tan \delta = \epsilon'' / \epsilon'$ characterizes the attenuation of the electric field in a lossy material.

It is expected that heating, biological, and some effects due to non-ionizing radiation depend on the "penetrating power" of the radiation and the latter is expected to peak in the microwave region as shown in Figure 2.2.1 (Tinga 1970). Because materials at low frequency highly reflect the incident energy and at high frequencies the energy is absorbed near the surface of the object, the field in the center of the object is comparable to the outside field only in the microwave range.

When an electromagnetic wave is incident on a lossy dielectric material, some radiation is reflected in optical fashion and some is transmitted into the subsurface with an change of direction (refraction) (Fig.2.2.2). The energy transmitted into the subsurface, however, is progressively absorbed or attenuated so that the wave decreases in magnitude as it penetrates into the material. Figure 2.2.3 gives the generalized physical model for microwave power absorption (Rich and Mudgett 1982).

The degree of absorption, reflection, and penetration for a particular material in microwave processing depends on its dielectric properties, i.e., dielectric constant and loss tangent $\tan \delta$. It is the dielectric constant which relates the value of the electric field within the material to the value of the electric field externally applied to the material which determines the reflection properties and the wavelength of the microwave radiation in the material. If the wave is normally incident (perpendicular to the material surface) then the reflected power related to the incident power is approximately given by the following equation:

$$P_{\text{refl}} / P_{\text{inc}} = \left[\frac{1 - \sqrt{\epsilon}}{1 + \sqrt{\epsilon}} \right]^2$$

The loss tangent $\tan\delta$ is a measure of the half-power penetration depth D : the depth at which the power level of the wave is decreased by 50 percent. For a given material this relationship is given by the following equation:

$$D = \frac{0.189 \lambda_o}{\sqrt{\epsilon} \sqrt{\sqrt{1 + \tan^2 \delta} - 1}}$$

From the above equations, it is seen that the larger $\tan\delta$, the smaller the penetration depth. And, also, the higher the dielectric constant, the lower is the value of D .

It is important to recognize that water, the physical structure of material, temperature, and several other factors will strongly affect the value of the dielectric properties.

The amount of moisture in a material can greatly affect the value of the dielectric constant because that water has a very high value of dielectric constant, approximately 80, whereas the base material has a dielectric constant of a much lower value, usually about 2.

Another important factor is temperature. The temperature dependence of dielectric constants can be quite complex. The rate of change of dielectric properties with temperature is a measurement of the activation energy of intermolecular and intramolecular displacements, rotations, bending, and twisting. Dielectric constants of materials may increase or decrease with temperature. At a specified frequency the temperature behaviour of a dielectric containing water is mainly dependent on the moisture content.

The physical structure of the material to be treated in a microwave system will also influence the interaction phenomena. Figure 2.2.4 shows the absorption cross-section of a sphere of material at approximately the microwave oven frequency of 2450 MHz as a function of the size of the sphere (Osepchuk 1975). It is observed that a moderate resonance is possible at around $2\pi a = \lambda/2$ but it is not very dramatic. Very small size objects absorb very inefficiently in a free field. To get a substantial cross section, $\lambda < 4\pi a$ is needed.

Additionally, density, frequency, conductivity, and specific heat, respectively, will also affect the value of dielectric properties. Therefore, it is extremely important to know in detail the functional relationships between these factors in any one material.

Generally speaking, the material will absorb the energy if it has any of the properties as follows (Tinga 1970): (a) a dipole which can rotate at the frequency of the incident radiation; (b) charges that can move at the frequency of the incident radiation; (3) magnetic domains that rotate at the frequency of the incident radiation.

For the mechanisms by which matter absorbs microwaves, the simplest explanation is that microwaves cause the molecules in matter to rotate and that the resulting friction produces heat. Actually, the microwave energy is transformed into heat by means of several complex conversion mechanisms such as (White 1973):

ionic conduction

interface polarization

- dipole rotation
 - entire molecule
 - quantized
 - twist
 - bend
- dipole stretching
- ferroelectric hysteresis
- electric domain wall resonance
- electrostriction
- piezoelectricity
- gas collision frequency resonance
- multifactor resonance
- cyclotron resonance
- nuclear magnetic resonance
- paramagnetic resonance
- ferromagnetic resonance
- ferrimagnetic resonance
- antiferromagnetic resonance
- spin wave resonance
- magnetic domain wall resonance
- magnetostriction
- piezo magnetism

Some of those mechanisms occur only in an interface with a vacuum, some only in magnetic materials, some only in ferroelectric materials, some only in plasmas, and so on. The first two mechanisms on the list, however, are involved in almost all useful heating through the application of microwave energy.

2.3 THE BASIC PRINCIPLES OF SOIL CHEMISTRY

Chemicals possess certain structures and undergo various reactions because they seek to attain the state of lowest potential energy. The goal of all naturally-occurring environmental processes is maximum energy release. Soil is a mixture of numerous naturally-occurring inorganic and organic chemicals. The rules of chemical reactivity which apply to "pure" chemicals also apply to soil as well. Soil, like all systems, possesses potential energy and seeks to maintain a state of minimum potential energy. Some of soil processes are listed in Table 2.3.1 (James 1988).

TABLE 2.3.1 SOIL PROCESSES INVOLVED IN THE TRANSPORT, TRANSFORMATIONS, AND INTERACTIONS OF SOIL SOLID

Process	Description
Alkalization	Accumulation of sodium ions and salts in a soil horizon.
Braunification	Release of iron from primary minerals.
Calcification	Accumulation of calcium carbonate in a soil horizon.
Cumulization	Addition of minerals at soil surfaces due to aeolian and hydrologic depositions.
Dealkalization	Migration of sodium ions and salts from natric horizons.
Decalcification	Removal of calcium carbonate from a soil horizon.
Decomposition	The breakdown of minerals and organic matter.
Desalinization	Removal of soluble salts from salic soil horizons.
Eluviation	Movement of solids and salts out of a soil.
Enrichment	Addition of solids and salts to a soil.
Erosion	Removal of solids and salts from a soil surface.
Gleization	The reduction of iron under anaerobic environments. Results in development of bluish to greenish gray soil colors, and possibly (a) yellowish brown, brown, and black mottles, and (b) iron and manganese-iron concretions.
Humification	Transformation of soil organic matter into humus.
Laterization	Movement of silica out of soil, resulting in a soil whose mineralogy is dominated by sesquioxides and possibly laterite, plinthite, and concretions.
Lessivage	Mechanical migration of small mineral particles from topsoil into subsoil, producing a relatively enriched clay horizon.
Leucinization	Lightening or paling of soil color due to the disappearance of organic matter.
Littering	Accumulation of organic matter and humus on the surface of mineral soil.
Melanization matter.	Darkening of soil by addition of organic

Mineralization	The release of mineral oxides through organic matter decomposition.
Pedoturbation	Churning and cycling of soil via biological and physical processes (e.g. freeze-thaw cycles, wet-dry cycles).
Podzolization	The migration of aluminum, iron, and/or organic matter, resulting in higher silica concentrations in the eluviated horizon.
Ripening	Alterations in the physical, chemical, and biological properties of organic soil due to aeration.
Salinization	Accumulation of soluble salts such as calcium, magnesium, sodium, and sulfates.
Synthesis	The formation of new minerals and organic matter.

2.3.1 Soil Heterogeneity And Soil Classification

The term soil is a collective noun that refers to a natural resource which resides at the earth's surface as a continuum of many different types of soils. These different soil types result from the action of climate on a parent material which has been modified by the influence of vegetation, organisms, and other factors over some period of geologic time. These different soil types have a large spectrum of physical, chemical, and biological properties and reactivity. Two classification schemes are in widespread use in the U.S.A.: The Unified Soil Classification System (the USCS) and the U.S. Comprehensive Soil Classification System, which was developed by the Soil Staff of the U.S. Department of Agriculture (the USDA system). For the classification criteria, see Figure 2.3.1 (James 1988).

2.3.2 The Surface-reactive Solid Phases In Soils

The solid phases that exhibit surface reactivity in soils are to be found mainly in the clay fraction. The most important molecular structural units in the inorganic

polymers found in soil clays are the silica tetrahedron, SiO_4^- , and the octahedral complex MX_6^{m-6b} , comprising a metal cation, M^{m+} , and six anions, X^{6-} . Both of these units can polymerize to form sheet structure which can be classified into three layer types and five groups distinguished by the numbers of tetrahedral and octahedral sheets combined, as illustrated in Figure 2.3.2 and Table 2.3.2 (Garrison 1984).

TABLE 2.3.2. PHYLLOSILICATE GROUPS COMMONLY FOUND IN CLAY FRACTIONS OF SOILS

Group	Layer type	Chemical formula charge	coefficients			
			a	b	c	c''
Kaolinite	1:1	<0.01	-	-	-	-
Mica (illitic)	2:1	1.4-2.0	6.8	3	$c + c'' = 0.25$	
Vermiculite	2:1	1.2-1.8	7	3	0.5	-
Smectite *	2:1	0.5-1.2	8	3.2	$c + c' = 0.2$	
Chlorite	2:1 with hydroxide interlayer	Variable	2.4	8.4	0.5	1.5

* Principally montmorillonite in soil clays.

2.3.3 Soil Organic Matters

When one turns to the organic solids, the uncertainties regarding structural chemistry are more complex. It is, in fact, not possible to describe a developed molecular structure for these compounds at present, although something can be said about the precursors of such a structure. Collectively, the dark microbially transformed organic solid materials that persist in soils are termed humic

substances, and it is known that their synthesis involves phenolic compounds resulting from the decomposition of proteins and carbohydrates shown in Figure 2.3.3 (Garrison 1984). It is evident that many chemical and microbiological processes mediate the polymerizations leading to the formation of organic, surface-reactive solids from the precursors.

2.3.4 Adsorption Of Organic Chemicals On Soil

Knowledge concerning the adsorption of organic chemicals on soils is essential for the assessment of the fate of organic chemicals in the environment and for the assessment of potential adverse impacts. The extent to which an organic chemical is adsorbed is determined by the chemical's structure and the soil's physical and chemical properties.

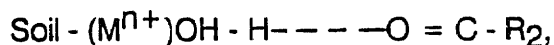
Chemical structure determines the magnitude of the organic chemical's gross properties such as molecular volume, water solubility, octanol-water partition coefficient, and vapor pressure that influence the overall adsorptive behavior of the chemical. Generally speaking, there are six aspects of chemical structure that govern adsorption (James 1988):

(1) Molecular size. First, the overall size of the organic molecule significantly influences its adsorption potential. In general, the larger the molecule, the greater its propensity to exist in the adsorbed state. The larger the molecule, the greater the contribution of Van der Waal's forces to the adsorption potential. As a general rule, Van der Waals forces become the dominant adsorption mechanism in non-sandy soil when the molecular weight of the organic chemical exceeds 400 - 500.

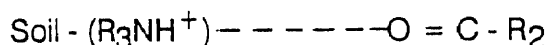
(2) Hydrophobicity. The second factor that affects organic chemical adsorption onto soil surfaces is the molecule's hydrophobicity or lipophilicity. The net hydrophobicity of any molecule is governed by the combined effect of hydrophobic and hydrophilic fragments that comprise the molecule. Although soil organic matter is usually implicated as the soil solid responsible for accumulating organic chemicals, it is most important to recognize that soil mineral surfaces also possess hydrophobic regions that can preferentially accumulate organic chemicals. Some research reveal that several inorganic particle surfaces, especially clay, have been found to govern the extent of adsorption of various organic chemicals (Find er al. 1970; Artiola et al. 1982; Doherty and Warren 1969). The organic matter in most soil is intimately bound to clay as a clay-organic complex. As a result, two major types of adsorbing surfaces are available to an organic chemical: clay-organic and clay alone. The relative contribution of organic and inorganic surface areas to adsorption will depend upon the extent to which the clay is coated with organic matter. The influence of clay on organic chemical adsorption can be significant, especially in soils with organic matter contents below one percent (Erler et al. 1983)

(3) Molecular charge. The third factor that affects organic chemical adsorption onto soil surfaces is the intrinsic positive or negative charge possessed by some organic molecules.

(4) Hydrogen bonding. The fourth factor is hydrogen bonding. There are three distinct types of hydrogen bonding which can occur between organic molecules and soil particle surfaces (James 1988). The first is the formation of a hydrogen bond via the linking of a polar organic molecule to an adsorbed cation through a water molecule in the cation's primary hydration shell:



which has been identified for montmorillonite systems containing pyridine, acetone and other ketones, benzoic acid, nitrobenzene, amides, and organic polymers (Mortland 1970; Farmer and Mortland 1966). The second type of hydrogen bonding can occur between an adsorbed organic cation and another organic molecule:



The strength of this type of bond depends upon the relative basicity of the neutral organic molecule. The third type of hydrogen bonding can occur between organic molecule fragments and the oxygen and hydroxyl groups on the surface of soil particles.

(5) Arrangement and Interaction of Molecular Fragments. The three-dimensional arrangement of the molecular fragments that comprise an organic chemical also can have a significant effect on its adsorption potential.

(6) Coordination. The final factor that affects organic chemical adsorption onto soil surfaces is coordination. For example, infrared studies have revealed that the oxygen of the nitro group on nitrobenzene can displace coordinated water molecules and become directly coordinated to adsorbed K^+ and NH_4^+ (Yariv et al. 1966). In another study, acetone adsorption at bentonite surfaces occurred through coordination between the carbonyl oxygen and adsorbed Na, Ca, Mg, Al, Cu, and NH_4^+ (Parfitt and Mortland 1968).

2.3.5 Soil Water

Soil water is a very important factor in the soil chemistry. Water exists on the surface of soil aggregation as a film. Some of functions of soil water were mentioned above. There are two major kinds of water between the soil aggregations: adhesion water and cohesion water. Adhesion water is referred to as layers of water molecules which are strongly adsorbed to the soil aggregation because of their adhesion forces. Cohesion water is referred to as water molecules which are held in the water films because of hydrogen bonds. Adhesion water, compared to cohesion water is held stronger, therefore, such water is less mobile (Iwata, Tabuchi, and Wakentin 1988).

2.4 A SURROGATE FOR DIOXIN: 9, 10 - ANTHRAQUINONE

There are many members of the dioxin class of chemicals. Among them, 2,3,7,8-tetrachlorodibenzo-dioxin is considered by far the most toxic. Dioxin-contaminated soil is a serious problem. Currently there is no available technology to treat soils contaminated with dioxin. EPA has investigated land disposal and incineration of dioxin-contaminated soil (EPA 1986; EPA-600/2-80-197) and found that the greatest risk to human health results from the excavation and transportation of dioxin-contaminated wastes. Therefore, in-situ remediation technologies, among which microwave treatment is, are needed urgently to be developed. In order to study the applicability of microwave technology to remediate TCDD-contaminated soil, a non-toxic compound, anthraquinone with similar properties, was chosen as a surrogate compound for the initial studies (Gu 1989).

9,10 - anthraquinone is a polyaromatic, insoluble, non-volatile compound and has some properties similar to the TCDD (Gu 1988). Anthraquinone has some properties as follows (Merck Index 1976; Kirk-Othmer 1986; EPA 1984; CRC. Handbook, 1986/1987; Lenga 1986):

(1) Identification

CAS number: 84-65-1

NIOSH number: CB4725000

Synonyms: 9,10-Anthraquinone, 9,10-Anthracenedione,
Anthradione, and 9,10-Dioxoanthracene

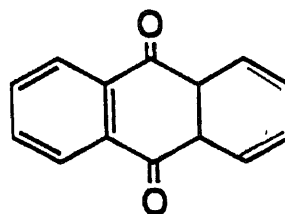
(2) Physical Properties

Empirical formula: $C_{14}H_8O_2$

Structural formula: C = 80.76%

H = 3.87%

O = 15.37%



Molecular weight: 208.25

Melting point: 283.5 - 285 °C

Boiling point: 379 - 381 °C

Flash point: 185 °C

Decomposition temperature: 450 °C

Vapor pressure: 10.0 Kpa at 286 °C, 20.0 Kpa at 300 °C,
and 48.0 Kpa at 340 °C

Density of the crystals at 20 °C: 1.438 g/cm

Density of the melt at 293 °C: 1.067 g/cm

Enthalpy of formation: -179 KJ/mol

Enthalpy of combustion at 25 °C: 6449 KJ/mol

Melting enthalpy at 287 °C: 32.57 KJ/mol

Molar heat capacity (Cp, solid): 265 J mol K

Solubility in water: Insoluble (0.006 g/l at 50 °C)

Solubility in organic solvents:

0.05 g/100 g ethanol at 18 °C

2.25 g/100 g ethanol at 78 °C

0.19 g/100 g toluene at 15 °C

2.56 g/100 g toluene at 15 °C

The UV spectrum: 251 nm (E_{max} 54000),

279 nm (E_{max} 17600)

321 nm (E_{max} 4800),

377 nm (E_{max} 110)

The IR spectrum: 1680 cm⁻¹ (C=O bond)

1600 cm⁻¹ and 1587 cm⁻¹ (aromatic double bond)

(3) Chemical properties

Anthraquinone exhibits extraordinary thermal stability, even in the presence of oxidizing agents; it is attacked by oxidizing agents only under vigorous conditions. On the other hand, anthraquinone can be reduced easily by ordinary reducing agents or by hydrogen in the presence of catalyst.

(4) Toxicological effects

Low systemic toxicity; may be harmful by inhalation, ingestion; or skin absorption cause irritation.

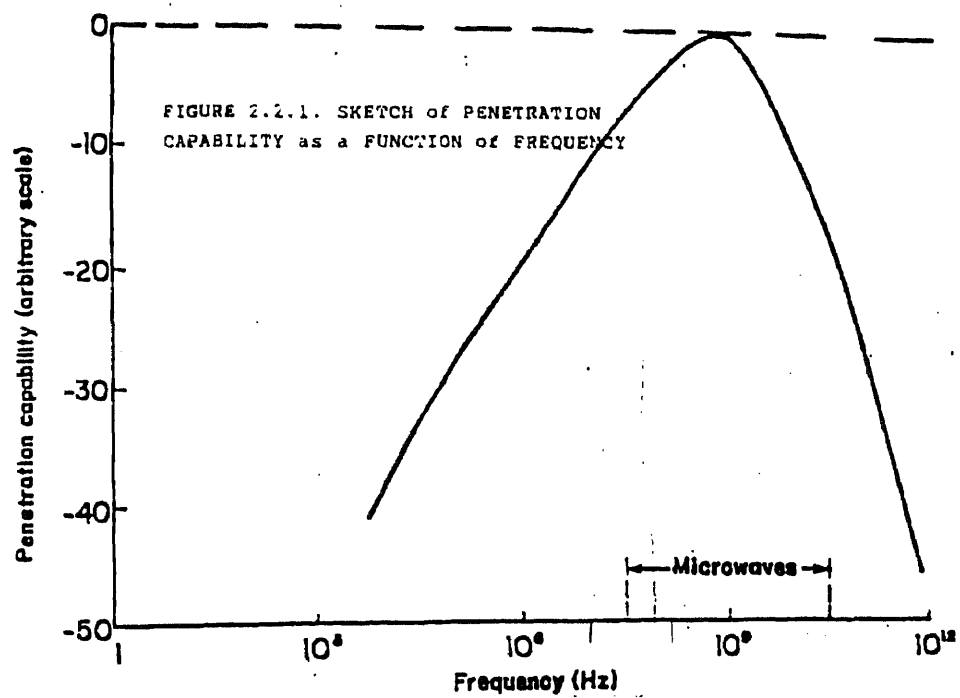
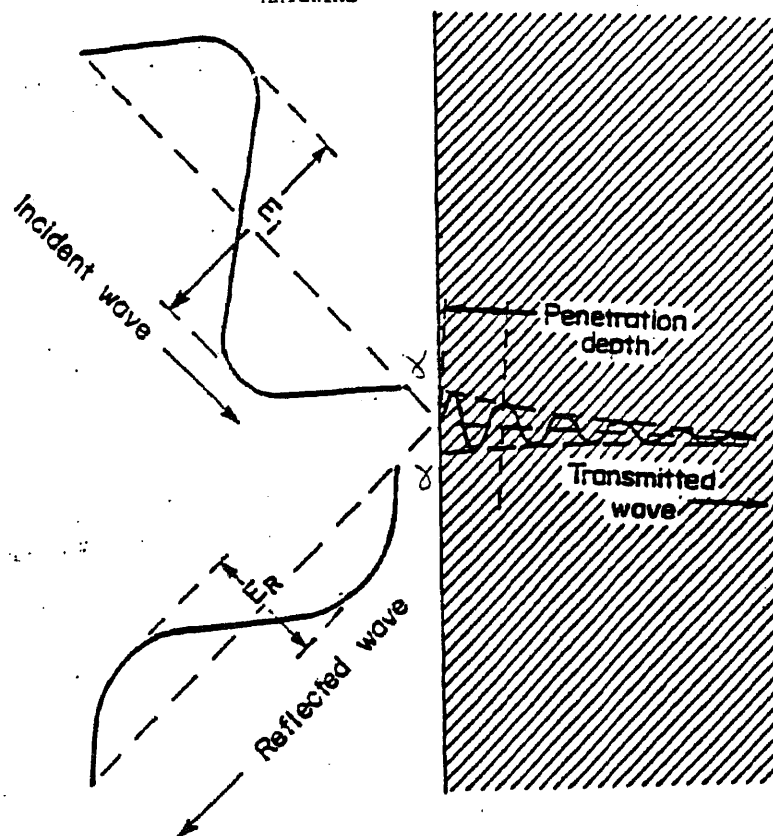


FIGURE 2.2.2. A PLANE WAVE INCIDENT on a LOSSY DIELECTRIC MATERIAL



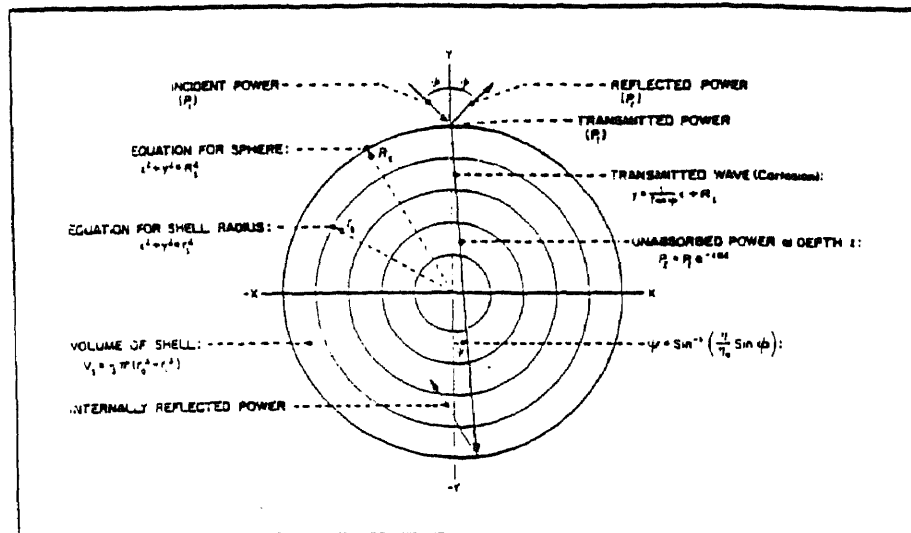


FIGURE 2.2.3. GENERALIZED PHYSICAL MODEL for MICROWAVE POWER ABSORPTION BY a SPHERE

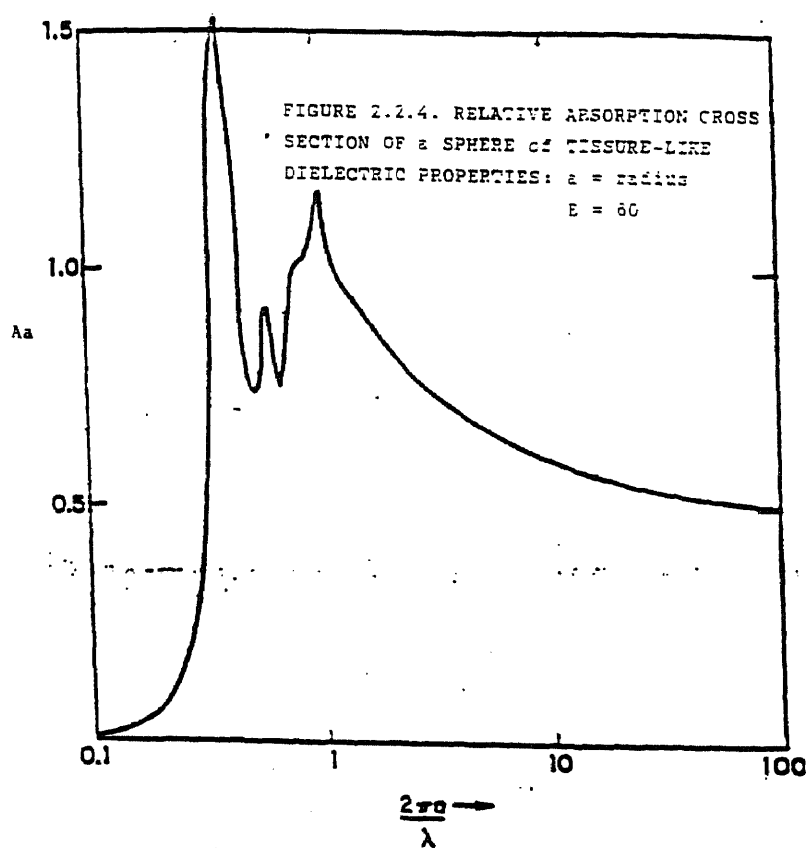
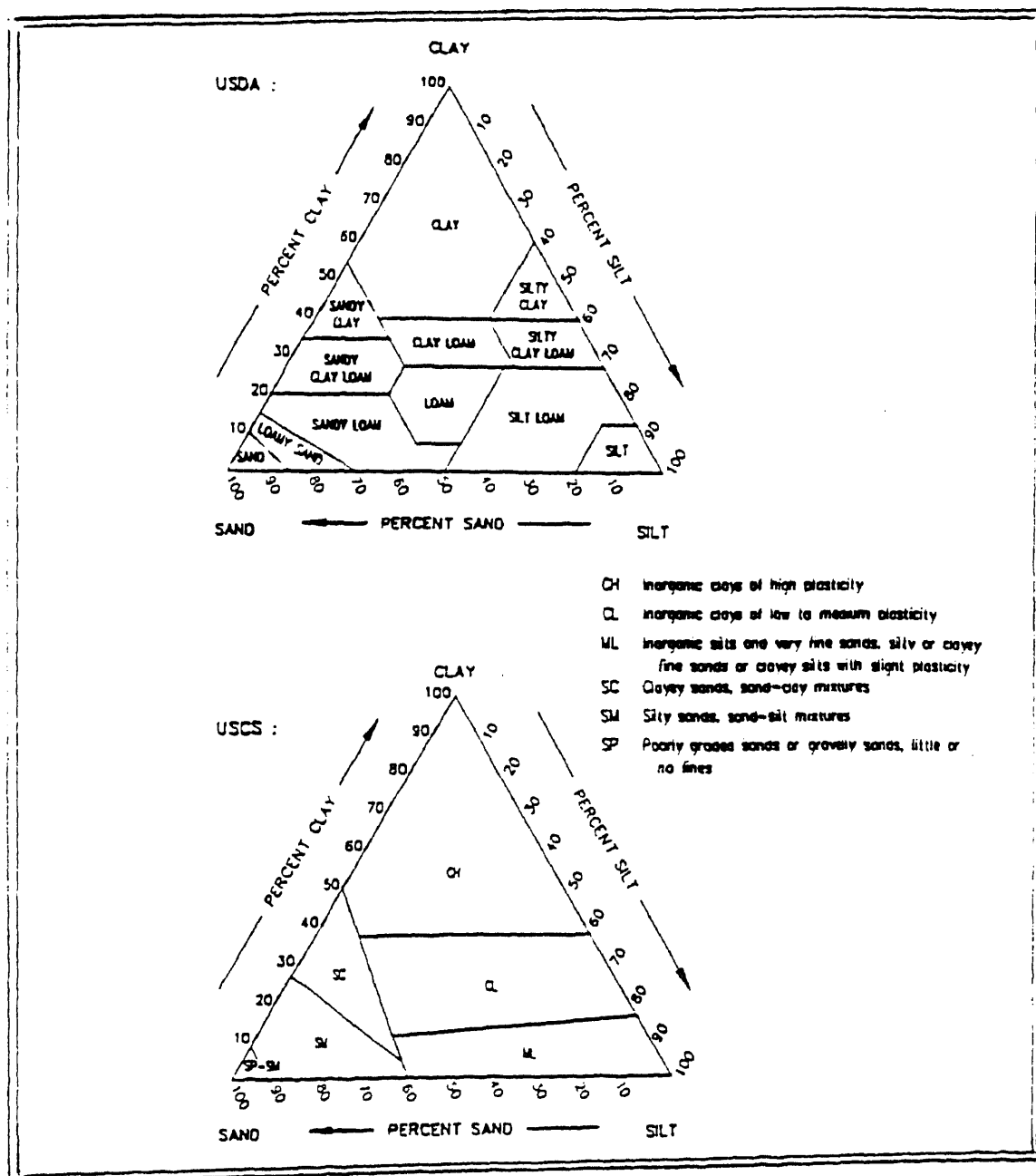


FIGURE 2.3.1. TEXTURAL TRIANGLES for the USDA and USCS
SOIL CLASSIFICATION SYSTEMS



CHAPTER 3. EXPERIMENTAL SERIES I

USING MICROWAVE ENERGY TO TREAT ANTHRAQUINONE-IMPREGNATED SANDY SOIL

3.1 INTRODUCTION

Previous studies have shown that microwave technology can be used to treat non-volatile organic-contaminated soils. Those studies were carried out mainly on clay soil, and to a lesser extent on sandy soil. The aims of this phase of the study were as follows: the application of microwave technology to the treatment of sandy soil impregnated with an insoluble non-volatile organic chemical, namely, anthraquinone; the application of GC/MS to the analyses and detection of the organics in the extracts from the contaminated soil; and selection of the optimum treatment conditions.

3.2 EXPERIMENT

3.2.1 Instrumentation

The organics in the extracts from contaminated soil can be analyzed by GC/MS. GC/MS is the combination of the two powerful analytical techniques. Gas chromatography is the physical separation of two or more compounds based on their differential distribution between two phases. A mass spectrometer is one kind of GC detector in the GC/MS. As the separated sample component molecules elute from the column to the inside of the MS they are bombarded with electrons. This causes them to lose an electron. Ions are formed with a positive

charge. A mass spectrum is a recording of the masses of each of the ionized fragments, a presentation of a unique fingerprint of molecules that can be used in identification. Mass spectrometry can be used to detect and quantitate compounds in concentrations of only a few parts per billion.

The instruments and operating conditions used in this study were as follows:

(1) Microwave Oven: SHARP, #CAROUSEL II.

The microwave treatment was conducted in a modified domestic microwave oven: 2450 MHz, 700 W.

(2) GC/MS: Hewlett-Packard 5890/5970 GC/MS with 59970 ChemStation

The 5890 Gas Chromatography used has a splitter (4.5 : 1). An HP-1 capillary column (PONA 12.0m X 0.2mm X 0.33 μ m) was chosen to improve the separation and 1.0 μ l of solution was injected. The data processing system utilized in the HP 59970 ChemStation included the NBS library with mass spectra of 38,000 compounds.

(3) Thermocouple: GLAS-col MODEL PR-800

The measurements were carried out immediately after shutting off the microwave oven.

(4) Soxhlet extractor: 34-mm I.D., with 125-ml round-bottom flask.

Ultrasonik: NEY model 300

3.2.2 Materials

The materials used in the study were as follows:

(1) Sandy soil

Sandy soil from South Mountain Reservation in New Jersey was chosen for the experiment. The properties of this kind soil are as follows according to a previous study (Gu 1990):

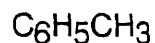
- * The moisture content is 8.5%;
- * The pH of soil is 6.5-7.0;
- * The clay content is 9.9%;
- * The metal elements contents: $\text{Ti} = 0.29\% \pm 0.01$ (wt/wt)
 $\text{Mn} = 147 \pm 8$ ($\mu\text{g/g}$)
 $\text{Fe} = 2.10\% \pm 0.01$ (wt/wt)
 $\text{Cu} = 56 \pm 3$ ($\mu\text{g/g}$)
 $\text{Zn} = 169 \pm 10$ ($\mu\text{g/g}$)

(2) Toluene

Toluene used in the study was manufactured by EM SCIENCE, INC.

The relevant information is as follows:

- * CAS number: 1-8-88-3
- * Chemical structure:



* Density: 0.8669 g/ml (CRC)

* Spectral charaters (UV-VIS):

(nm)	350	300	288	286	285
A	0.003	0.091	0.332	0.532	0.712

(3) Anthraquinone

Anthraquinone used in the study was manufactured by Matheson, Coleman and Bell.

The properties of anthraquinone are listed in Chapter 2.

3.2.3 Experimental Procedure

Step 1. A solution of 9,10-anthraquinone in toluene was prepared. Anthraquinone, 0.867 gram, was diluted with toluene to 500 ml. The concentration of the solution was 2000 ppm.

Step 2. A calibration curve of anthraquinone solution was prepared in the range from 40 ppm to 2000 ppm for the quantitation of extract from the sample using GC/MS.

Step 3. The ambient moisture level of sandy soil sample was determined. The sample was kept at ambient conditions (air conditioned laboratory) over 48 hours to reach ambient humidity, put in the thermal oven 48 hours at 110 °C, and weighed before and after heating.

Step 4. The extracts from sandy soil for the background were prepared. Two 50 gram soil samples were extracted in the Soxhlet extractor for 24 hours using 50 ml toluene and diluted to 50 ml. Meanwhile, another two 50 gram soil samples were extracted with 50 ml toluene in an ultrasonic bath for 20 min, vacuum filtered, and diluted to 50 ml. For the analysis, 1.0 μ l extract from each samples was injected into the GC/MS using parameters from the previous study (Gu 1990).

Step 5. Sandy soil samples were impregnated with anthraquinone. First, 25 ml of anthraquinone solution was added to each soil sample, and then samples were placed in a hood for 24 hours to evaporate the toluene. The theoretical concentration in each sample was 1000 ppm.

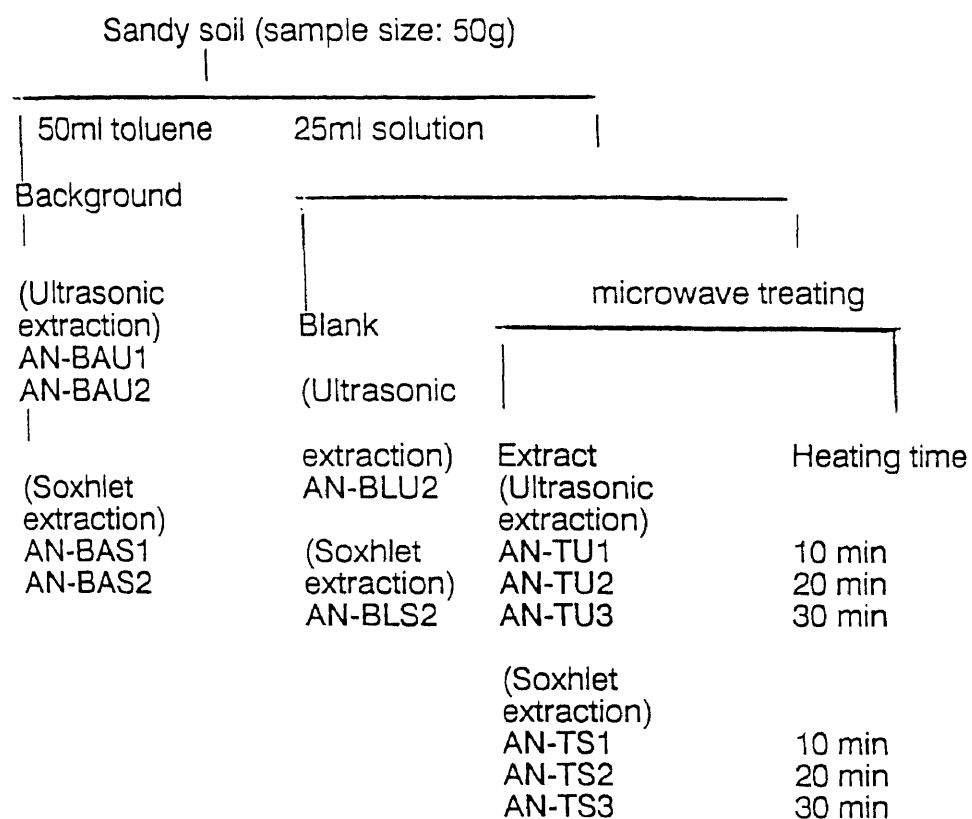
Step 6. The extracts (blank) from anthraquinone-impregnated soil were obtained with 50 ml toluene using Soxhlet extractor and Ultrasonic extraction, respectively. The amount of anthraquinone extracted from the blank was considered as the 100% reference amount.

Step 7. The samples of anthraquinone-impregnated soil were treated in a microwave oven for 10 min, 20 min, and 30 min, respectively, after prewarming the microwave oven for 10 min with about 500 ml water. After treatment, samples were extracted with Soxhlet or Ultrasonic extraction in the way previously described to carry out the blank extractions. All samples were put in the glass beakers with a surrounding sand bath which acted as an insulator during the treatment, but which was translucent to microwave radiation.

To each sample, 5 ml of distilled water was added before extraction.

The sample designations and different experimental conditions are summarized in Figure 3.1.

FIGURE 3.1. THE DESIGNATIONS AND CONDITIONS



3.3 EXPERIMENTAL DATA AND RESULTS

3.3.1 The Ambient Moisture Level Of Sandy Soil

Before heating the weight of sandy soil was 80.167 g. After heating the weight of sandy soil was 79.722g. The ambient moisture level was:

$$(80.167 - 79.722) / 80.167 = 0.56\%$$

3.3.2 Microwave treatment of sandy soil

(1) Total ion chromatogram and mass spectrum of anthraquinone is shown in Figure 3.2.

(2) The calibration curve of anthraquinone is shown in Figure 3.5.

(3) In the background samples, no new compound was detected by GC/MS. Experimental raw data are listed in Appendix II.

(4) The results of the experiments in which the concentration of anthraquinone in the soil extract and the results of C/Co (the concentration of anthraquinone in the extract after treatment / the concentration of anthraquinone in the extract before treatment), measured by GC/MS, as a function of the microwave heating time, are shown in Table 3.1 and Table 3.2.

TABLE 3.1. C/Co IN SOIL EXTRACT vs. MICROWAVE HEATING TIME
(ULTRASONIC EXTRACTION)

Sample	Heating Time	Concentration	C/Co	Extractability
AN-BLU2	(blank)	842.5 ppm	1	842.5/1000 = 84%
AN-TU1	10 min	589.1 ppm	0.70	
AN-TU2	20 min	267.1 ppm	0.32	
AN-TU3	30 min	262.5 ppm	0.31	

TABLE 3.2. C/C₀ IN SOIL EXTRACT vs. MICROWAVE HEATING TIME
(SOXHLET EXTRACTION)

Sample	Heating	Concentration	C/Co	Extractability
AN-BLS2	(blank)	946.8 ppm	1	946.8/1000 = 95%
AN-TS1	10 min	834.7 ppm	0.88	
AN-TS2	20 min	387.8 ppm	0.41	
AN-TS3	30 min	300.5 ppm	0.32	

4. DISCUSSION AND RECOMMENDATION

(1) From the experiment, it is known that ambient moisture level was just 0.56%. This value obviously is too low based upon a comparison with the value reported by Gu in the previous study. A possible reason may be that moisture in the soil was lost when the soil sample was exposed in the air conditioned room for five days. Therefore, future measurements of the moisture level of soil were carried out without the soil being exposed in the air conditioned room.

(2) From Table 3.1, Table 3.2, Figure 3.3, and Figure 3.4, it is observed that, after microwave treatment, the concentration of anthraquinone in the soil extract dropped rapidly in the first 20 min. Then decreased slowly. Sand, that is, quartz or silica, which is present in a higher level in sandy soil, is a poor microwave absorber; therefore the temperature does not increase sufficiently to immobilize the remaining anthraquinone. In this series of experiments, temperature measurements were not carried out. Temperature is a very important factor in the treatment. In the next series of experiments to be reported upon, temperature measurements were carried out to determine whether or not, in fact, the stopping of the immobilization of anthraquinone correlates with the plateauing of the temperature.

(3) By comparing the results of this experiment with those of previous study (see Table 3.3), it is found that the C/C_0 value in the previous study decreased much more rapidly than that in this experiment. The lowest C/C_0 value in the previous study, which was reached after 16 minutes heating time, was 2.2%. In contrast, the lowest C/C_0 value in this experiment was 31%. The value was reached after 30 minutes heating time. This difference may be due to the effect of water: the moisture level of sandy soil used in previous study was 8.5% (Gu 1990), while the moisture level of sandy soil used in this experiment was 0.15% (sandy soil was put in the air conditioned room for five days). Moreover, in this experiment, 5 ml of distilled water was added to each sample prior to extraction, but, in the previous study, no water was added. The above results suggest that water may play an important role during the whole process. Adding water before microwave treatment may not only help speed up the reduction of the concentration of anthraquinone but also it may aid in the reaching of a lower C/C_0 value. In

addition, adding water before extraction may increase the extractability of the anthraquinone. Besides, the difference in the lowest C/C_0 in the two studies may be due to experimental errors. It was concluded in the previous study, that "chemical fixation " may occur at about 200 °C for both sandy soil and clay soil; little anthraquinone could be detected for clay soil above 300 °C. From the data of the previous study, Table 3.3, it is seen that the temperature was about 220 °C when the heating time was 15 minutes and the C/C_0 value was 2.2%. It seems improbable that such a low C/C_0 was reached at such a low temperature. In addition, it is also observed that the amount of anthraquinone detected by GC/MS was decreased by nearly half when the heating time was 2 minutes, corresponding to a temperature of 127 °C. Those results are apparently contradictory. The following experiments were carried out to answer these concerns.

(4) Recommendations for the following experiment:

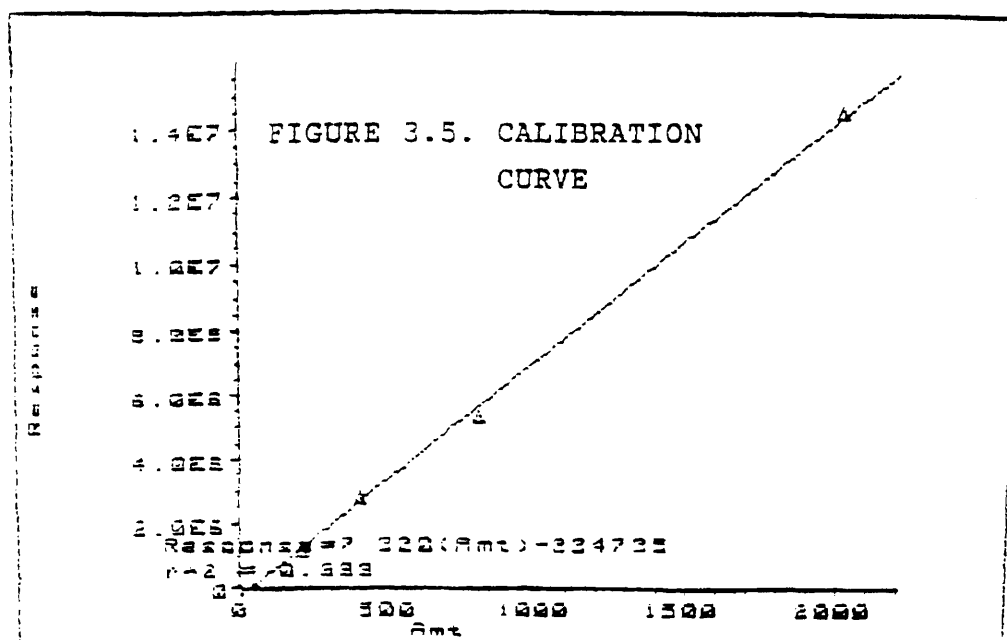
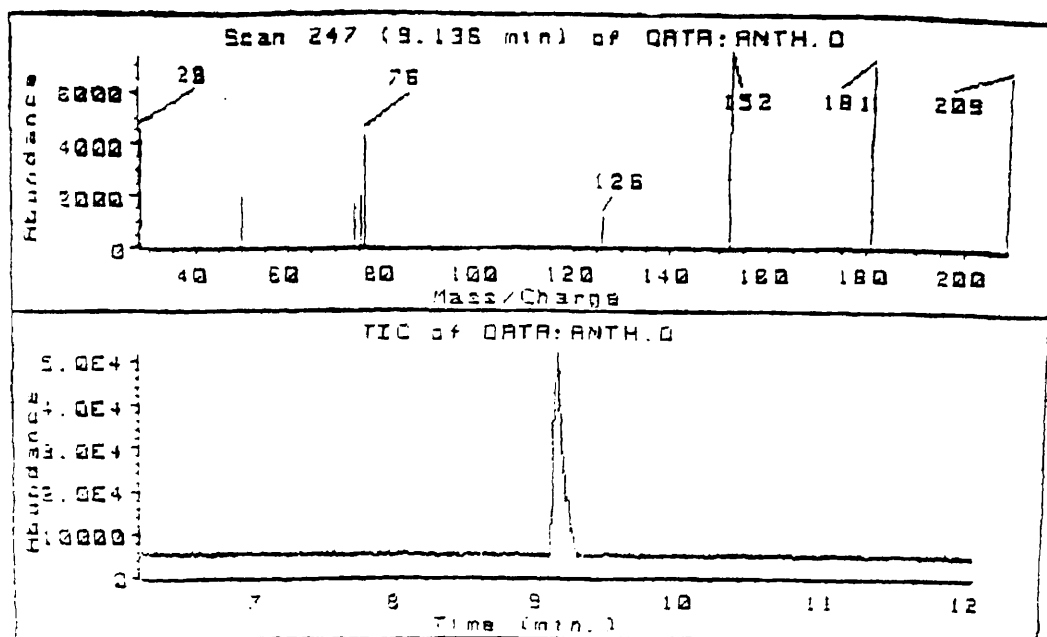
(a) Determine the effect of water on microwave treatment of soil samples as follows: to one series, water would be added before microwave treatment; to the other, no water would be added.

(b) Determine the effect of adding water to soil samples prior to extraction: to one series, water would be added; to the other, water would not be added preceding extraction.

TABLE 3.3 C/C₀ IN SANDY SOIL SOIL EXTRACT vs. MICROWAVE HEATING TIME [from the previous study (Gu 1990)]

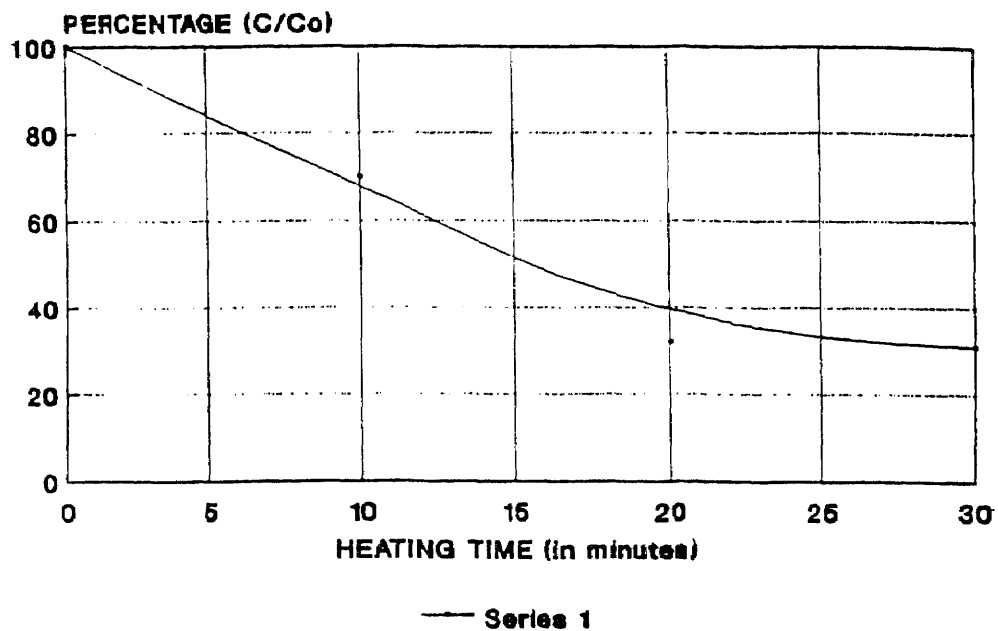
Heating time	Temperature	C/C ⁰
2 min	138 °C	67.5
4 min	190 °C	7.5
6 min	200 °C	4.6
8 min	217 °C	2.6
10min	225 °C	-
15min	200 °C(without sandbath) -	-
16min	-	2.2

FIGURE 3.2. TOTAL ION CHROMATOGRAM
AND MASS SPECTRUM OF ANTHRAQUINONE



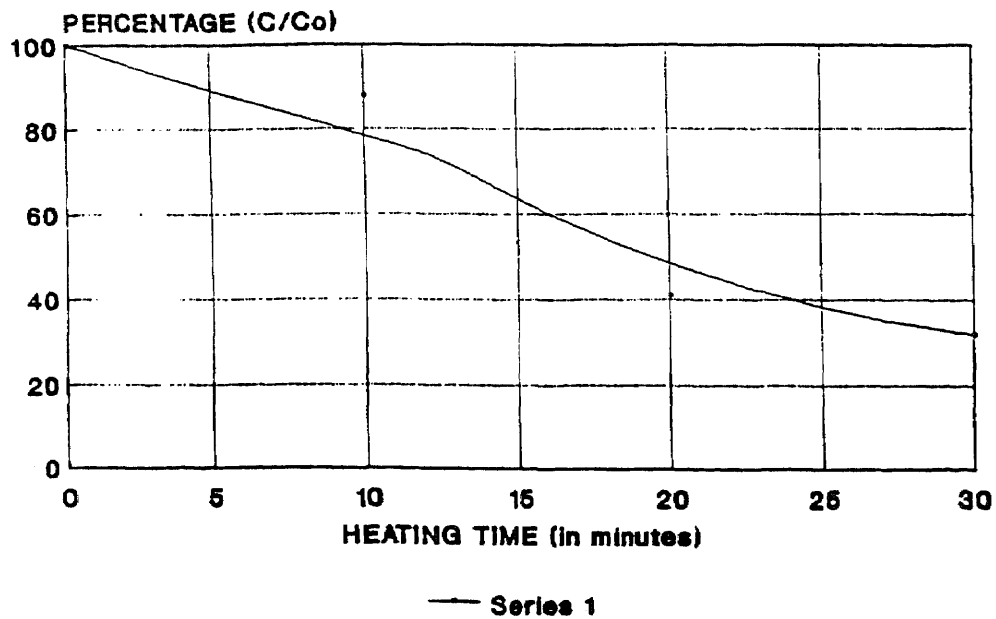
Ret Time	Pk#	Signal Descr	Amt ng/ui	Lvl	[Area]	Pk-Type
9.455	1	207.00- 210.00 amu	40.00	1	8678	1
			200.0	2	1168901	
			400.0	3	2790129	
			800.0	4	5271393	
			2000	5	14531860	

**FIGURE 3.3 THE C/C_0 IN SANDY SOIL
EXTRACT vs. MICROWAVE HEATING TIME**



ULTRASONIC EXTRACTION

**FIGURE 3.4 THE C/C_0 IN SANDY SOIL
EXTRACT vs. MICROWAVE HEATING TIME**



SOXHLET EXTRACTION

CHAPTER 4. EXPERIMENT SERIES II

MEASUREMENT OF MOISTURE LEVEL OF SOIL

4.1 INTRODUCTION

The objective of this experiment was to determine the present moisture of sandy soil and clay soil, respectively.

The determination of the percent moisture of soil was carried out by drying soil samples in a convection oven for 48 hours at 110⁰C and then cool in the samples in a desiccator before weighing:

$$\frac{\text{g of sample} - \text{g of dry sample}}{\text{g of sample}} \times 100\% = \% \text{ moisture}$$

4.2 EXPERIMENT AND RESULTS

4.2.1 Sandy Soil

Four samples of sandy soil were taken from the bag (the brown sandy soil was dug from South Mountain Reservation in New Jersey) and weighed. After weighing, samples were put in the thermal oven for 48 hours at 110⁰C. Results are shown in Table 4.1.

TABLE 4.1. THE MOISTURE LEVELS OF SANDY SOIL

No.	Weight before heating	Weight heating 24hr	Weight heating 48hr	Moisture%
1	73.6	-	71.5	2.9
2	74.1	71.8	71.8	3.1
3	72.1	70.0	70.0	2.9
4	71.0	68.8	68.8	3.1

4.2.2 Clay Soil

The measurement of moisture level of clay soil was also based on the weight difference before and after soil was heated in an oven for 48 hours at 110 °C. Results of experiment are listed in Table 4.2.

TABLE 4.2. THE MOISTURE LEVEL OF CLAY SOIL

No.	Weight before heating	Weight heating 24hr	Weight heating 48hr	Moisture%
1	87.6	-	80.0	8.7
2	86.3	79.8	79.8	7.5
3	87.9	-	81.1	7.7
4	90.0	82.9	82.9	8.6

4.2.3 Conclusions

- (1) The average moisture level of sandy soil was 3.0%.
- (2) The average moisture level of clay soil was 8.1%.

4.3 DISCUSSIONS

(1) From Table 4.1 and Table 4.2, it is observed that there is no significant difference between 48 hour heating time and 24 hour heating time concerning results of drying. Therefore 24 hours is sufficient to measure the moisture level of soil.

(2) In this experiment, the moisture level of sandy soil was 3.0% and the moisture level of clay soil was 8.1%. In the previous study (Gu 1990), the moisture level of sandy soil was 8.5% and the moisture level of clay soil was 4.9%. The value of moisture content varies greatly because of different conditions. It is suggested that the moisture level be measured before every batch experiment in order to interpret the results properly.

(3) The moisture content of soil is a critical factor in determining the relative contributions of mineral and organic soil fractions to soil uptake of nonionic organic compounds. To assess the impact of moisture on anthraquinone sorption, The following experiment for the sorption of anthraquinone on the soil was carried out as a function of relative humidity.

CHAPTER 5. EXPERIMENTAL SERIES III

COMPARISON OF EXTRACTABILITY OF TWO EXTRACTION METHODS

5.1 INTRODUCTION

In this experiment, one objective was to compare the extractability of anthraquinone in the extracts by two extraction methods: Soxhlet extraction and Ultrasonic extraction. Another, to assess the effect of water on extraction.

5.2 EXPERIMENTAL THEORY

Soxhlet extraction and Ultrasonic extraction were used, respectively, to extract anthraquinone from the anthraquinone-impregnated soil samples before and after microwave treatment in this study.

Soxhlet extraction is a multistage mass transfer operation. If a compound has a limited solubility in the selected solvent, then a continuous process is appropriate. For this purpose a Soxhlet extractor is the apparatus of choice. The soil sample is placed in a cellulose thimble. The thimble is then placed in the extraction chamber, which is fitted to the boiling flask and condenser. The solvent is boiled, whereupon the vapors travel upwards into the condenser via the vapor bypass. The condensed liquid is returned to the extraction chamber where it comes in contact with the solid sample to be extracted. When the chamber fills to the level of the top of the siphon tube on the side of the apparatus, the solution then drains back into the boiling flask because of the siphon action. As long as the boiling

flask is heated, the process can continue indefinitely. The result is the gradual dissolution and ultimate separation of the desired compound from the solid mixture.

Ultrasonic extraction is an extraction method in which cavities, formed by sound pressure waves, collapse in the fluid; the collapse of the cavity causes shock waves which create maximum contact between the fluid and the soil sample.

5.3 EXPERIMENT

5.3.1 Instruments And Experimental Conditions

Soxhlet extractor: 34-mm I.D., with 125 ml round-bottom flask. A fifty ml of solvent toluene was used and a forty gram sample was placed in a cellulose thimble (25 x 80 mm). The extraction time was 24 hours. After extraction, the extract was diluted to 50 ml.

Ultrasonic: NEY model 300. Fifty ml of solvent was used. Extraction time was 20 minutes; the water bath was at ca. 45 °C. After extraction, the sample was filtered by vacuum filtration (Buchner funnel) and then was diluted to fifty ml with toluene.

GC/MS: The organics in the extracts were analyzed by the Hewlett-Packard 5890/5970 GC/MS with 59970 ChemiStation software.

5.3.2 Design Of The Experiment

(1) Two solutions of anthraquinone were prepared in toluene. The concentration of solution 1 (ANSL2), which was measured by GC/MS using the calibration curve in the experiment series I, was 2020.5 ppm; another (solution 2:ANSL3), was 2963 ppm.

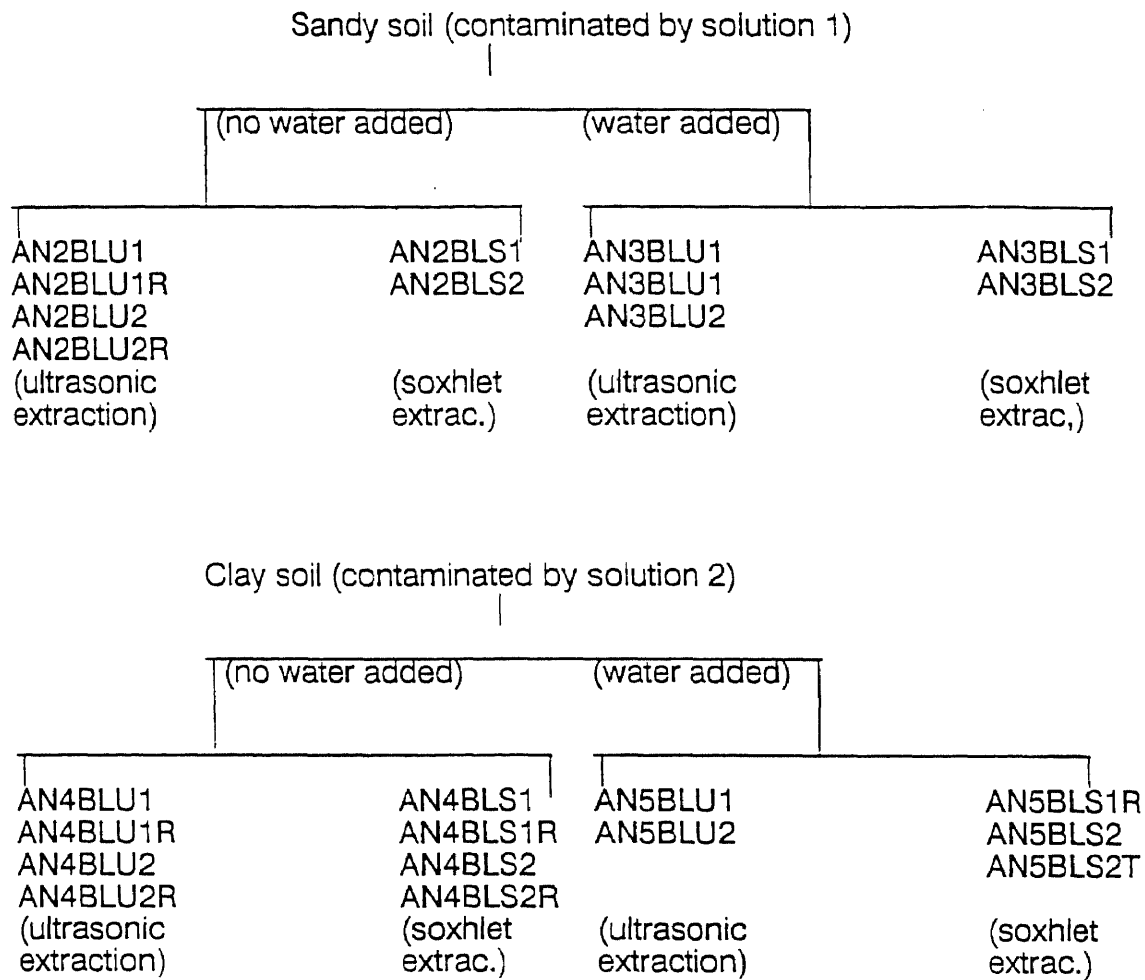
(2) 25 ml of the solution was pipetted into 40 gram soil samples (clay soil and sandy soil), mixed, and then the solvent was evaporated for 24 hours under the hood.

The concentration of anthraquinone, after mixing 25 ml of solution #1 in 40 gram soil, was: $2020.5 \mu\text{g/ml} \times 25 \text{ ml} / 40 \text{ g} = 1261 \mu\text{g/g}$.

The comparable concentration of anthraquinone using solution #2 was: $2963 \mu\text{g/ml} \times 25 \text{ ml} / 40 \text{ g} = 1852 \mu\text{g/g}$.

(3) The sample designations and the different experimental conditions are shown in Figure 5.1.

FIGURE 5.1 DESIGN OF EXPERIMENT



5.4 EXPERIMENTAL DATA AND RESULTS

5.4.1 Sandy Soil

The experimental data and results for sandy soil are listed in Table 5.1.

TABLE 5.1 EXTRACTABILITY OF SANDY SOIL SAMPLES

No.	Name of sample	Concentration(ppm)	Extractability
1	ANSL2	2020.5	
2	AN2BLU1	945.8	75 %
3	AN2BLU1R	951.5	75 %
4	AN2BLU2	867.1	69 %
5	AN2BLU2R	1006	80 %
6	AN2BLS1	1051	83 %
7	AN3BLU1	1142	90 %
8	AN3BLU1R	1091	86 %
9	AN3BLU2R	1214	96 %
10	AN3BLS1	1169	93 %
11	AN3BLS2	1234	98 %

5.4.2 Clay Soil

The experimental results for clay soil are listed in Table 5.2.

TABLE 5.2 EXTRACTABILITY OF CLAY SOIL SAMPLES

No.	Name of sample	Concentration(ppm)	Extractability
1	ANSL3	2963	
2	AN4BLU1R	919.3	50 %
3	AN4BLU2	999.6	54 %
4	AN4BLS2	1111.2	60 %
5	AN5BLU1	1276	69 %
6	AN5BLU2	1184	64 %
7	AN5BLS1R	1221	66 %
8	AN5BLS2	1353	73 %

5.5 CONCLUSIONS

5.5.1 Sandy Soil

(1) The average extractability by Ultrasonic extraction (no water to be added) is 75 %.

(2) The average extractability by Soxhlet extraction (no water to be added) is 83 %.

(3) The average extractability by Ultrasonic extraction (added water) is 91 %.

(4) The average extractability by Soxhlet extraction (added water) is 96 %.

5.5.2 Clay Soil

(1) The average extractability by Ultrasonic extraction (no water to be added) is 52 %.

(2) The average extractability by Soxhlet extraction (no water to be added) is 60 %.

(3) The average extractability by Ultrasonic extraction (added water) is 67 %.

(4) The average extractability by Soxhlet extraction (added water) is 70 %.

The calculated results are tabulated in Table 5.3 and Table 5.4.

TABLE 5.3 COMPARISON OF TWO EXTRACTION METHODS AND EFFECT OF WATER ON EXTRACTION (SANDY SOIL)

	Ultrasonic extractability	Soxhlet extractability	Increment of extractability
no water	75 %	83 %	8 %
water	91 %	96 %	6 %
increment of extrac.	14 %	13 %	

TABLE 5.4 COMPARISON OF TWO EXTRACTION METHODS AND EFFECT OF WATER ON EXTRACTION (CLAY SOIL)

	Ultrasonic extractability	Soxhlet extractability	Increment of extractability
no water	52 %	60 %	8 %
water	67 %	70 %	3 %
increment of extrac.	15 %	10 %	

5.6 DISCUSSION

(1) From Table 5.3 and Table 5.4, it is observed that, in all cases, Soxhlet extraction had higher extractability than Ultrasonic extraction. The value of the extractability increment was about 7 % for sandy soil and 6 % for clay soil. This is not considered to be a significant difference. Therefore, for general purposes, Ultrasonic extraction can be used because it is less time consuming. But, for some special analyses such as GC/FTIR, DRIFT, and etc, Soxhlet extraction may be preferable.

(2) In Table 5.3 and Table 5.4, it is also shown that extractability was affected by water. By adding water, extractability increased 14 % for sandy soil and 13 % for clay soil. This indicates that sorption of nonionic organic compounds decreases as soil moisture content increases. The natural soil functions as a sorbent for uptake and release of nonionic organic compounds. In the absence of water (polar molecules), nonionic compounds will occupy more of the soil binding sites. By contrast, in an aqueous system, a much stronger competitive adsorption of

water on the soil surface will result in suppression of the sorption of the organic compound. However, it is worth noting that natural soil actually functions as a dual sorbent. To assess the impact of moisture on nonionic compound sorption, both the mineral surface of the soil and the soil organic matter function should be considered. In the above discussion, the mineral surface of soil function is just considered. A more detailed study of the interactions of soil, water, individual organic in soil, and anthraquinone was carried out in subsequent experiments.

(3) In order to compare the extractability of sandy soil to clay soil, Table 5.5 was prepared from Table 5.3 and Table 5.4. In Table 5.5, it is shown that clay soil has a lower extractability. Compared with sandy soil extraction, the extractability of clay soil decreased 24 % (average). This is no surprise because of the higher surface area of clay soil and the special layer structure of clay. Clay soil, therefore, can absorb more non polar organic compound-anthraquinone than sandy soil.

CHAPTER 6. EXPERIMENTAL SERIES IV

MICROWAVE ENERGY TREATMENT OF ANTHRAQUINONE-IMPREGNATED CLAY SOIL

6.1 INTRODUCTION

The objective of this experiment was to find trends in the temperature of anthraquinone-impregnated clay soil system as a result of microwave treatment; in addition, to obtain extracts and clay soil after microwave treatment for further study by FTIR, DRIFT, ATR/FTIR, and other techniques.

6.2 EXPERIMENT

6.2.1 Instrumentation

A microwave oven, GC/MS, Ultrasonic, and thermocouple were used in this experiment. The models of the instruments and operating conditions in this experiment were the same as those described in the previous sections in this thesis.

The clay soil was taken from Aron Street, Middlesex County, NJ. The moisture level was 8.1 %.

6.2.2 Experimental Design

The experiment design was almost the same as the first experiment (experimental series I) except that water was not added before extraction in this study. The clay soil sample size was 40 grams. The concentration of anthraquinone solution was 2020.5 ppm (solution 1: ANSL2). Ultrasonic extraction was chosen because it is less time consuming. After microwave treatment, extracts of clay soil and soil samples treated and extracted were kept for the further study by FTIR, UV-VIS, ATR/FTIR, and DRIFT.

6.3 EXPERIMENTAL DATA AND RESULTS

The results tabulated in Table 6.1 show how the concentration of anthraquinone in the clay soil extract, and the C/Co (the concentration of anthraquinone in the extract after treatment / the concentration of anthraquinone in the extract before treatment), measured by GC/MS, vary with the microwave heating time.

TABLE 6.1 C/Co IN SOIL EXTRACTS vs. MICROWAVE HEATING TIME

No.	Name	Heating time	Concentration(ppm)C/Co	
1	AN4BLU2	BLANK	999.6	100%
2	1ANTR2	2 min	164.6	16 %
3	1ANTR2R	2 min	173.8	17 %
4	1ANTR4	4 min	60.24	6 %
5	1AMTR6	6 min	87.16	8.7%
6	1ANTR6R	6 min	81.11	8.1%
7	1ANTR8	8 min	0	0
8	1ANTR10	10min	0(45.27)*	0
9	1ANTR12	12min	0	0

* see discussion (5)

The effect of microwave heating time on temperature of clay soil is shown in Table 6.2.

TABLE 6.2 MICROWAVE HEATING TIME vs.
TEMPERATURE OF SOIL SAMPLE

No.	Heating time	Temperature (average)
1	2 min	150 °C
2	4 min	186 °C
3	6 min	210 °C
4	8 min	380 °C
5	10min	520 °C

6.4 DISCUSSIONS

(1) Table 6.1 and Figure 6.1 indicate that the percentage of anthraquinone in extracts from clay soil decreased with longer heating time. It is observed that, in the first 2 minutes, the percentage of anthraquinone dropped quickly. It is also observed that only 8.4% (average) was found in soil extracts after 6 minute microwave heating time, and no anthraquinone was found after 8 minute heating time. These results are almost the same as the results of the previous studies (Gu) in this lab.

(2) Table 6.2 and Figure 6.2 show that the measured temperature increased as the heating time increased. In the first 2 minutes, the temperature rose sharply, and then increased slowly and stably from 2 minutes to 6 minutes. After 6 minute heating time, the temperature increased quickly again. These results may be due to the following factors.

It is well-known that soil particles are held together in aggregates by water. But, anthraquinone is a hydrophobic compound which has no affinity for water. Anthraquinone is held to a surface by Van der Waal's forces and forms multilayers on the soil particles. When anthraquinone-impregnated clay soil was treated with microwave energy in the first 2 minutes, the charged particles, such as free ions and electrons, and the dipole material such as water, in the soil, absorbed microwave energy and increased the whole sample system temperature. After 2 minutes, the temperature reached 150 °C and no liquid water existed. At that time, the sample system absorbed microwave energy continuously. This might have resulted in the Van der Waal's bonds being broken and other bonds being formed, which could be due to the sorption of anthraquinone on the mineral surface of soil and organic matters in soil. In other words, at this period, some of microwave energy might be used by anthraquinone, and also some other organics which had existed in the soil, to break Van der Waal's bonds and to form new sorption bonds. Therefore no more energy could be used to increase the system temperature until 8 minutes had elapsed. After 8 minutes, most of anthraquinone had been fixed already in the soil (Figure 6.1 shows that no extractable anthraquinone could be found after 8 minutes). And then, the system temperature increased rapidly again.

(3) Recent scientific evidence indicates that soil functions as a dual sorbent for the uptake and release of nonionic organic compounds (Chiou and Shoup 1985; Chiou et al. 1988; Smith 1988). The mineral surfaces of the soil functions as a conventional solid adsorbent and the soil indigenous organics function as a partition medium. Mineral adsorption is characterized by vapor or solute condensation onto the mineral surface by physical and/or chemical bonding forces, whereas the partition uptake by soil indigenous organics is effected by

molecular forces common to solution, similar to the extraction of an organic solute by an organic solvent. A detailed sorption model (or fixation model) and mechanism can not be described based upon the data obtained in this study. But, the experimental results indicate that fixation of anthraquinone had occurred and that the sorption bonds were stronger than the Van der Waal's bonds because no extractable anthraquinone could be found in the soil. Experiments, to be described later, were carried out to obtain the data necessary to set up a sorption model.

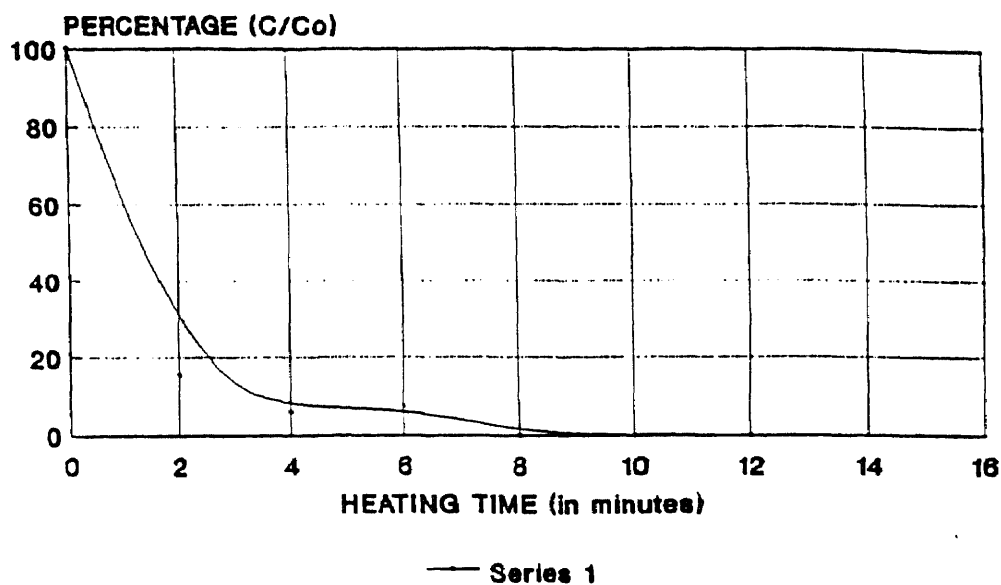
(4) From Figure 6.2, it can be inferred that the decrease of anthraquinone was not due to the decomposition, oxidation, and pyrolysis of anthraquinone in clay soil during the treatment by microwave energy. This conclusion is based on the following facts:

- (a) The boiling point of anthraquinone is 380°C .
- (b) The decomposition point of anthraquinone is 450°C .
- (c) In this experiment, the temperature was 150°C when the heating time was 2 minutes; the temperature was 185°C when heating time was 4 minutes; and temperature was 210°C when heating time was 6 minutes.

This study indicates that almost no anthraquinone could be found in extracts of soil after 8 minute heating time, but the temperature was still below decomposition point of anthraquinone. Besides, the previous study (Gu) also showed that no anthraquinone or volatiles were found in gas phase of sample. This means that no anthraquinone was in the liquid phase and no anthraquinone or volatiles in the gas phase. So it is assumed that anthraquinone is fixed in the soil. Further studies, to be reported, were carried out to get more direct evidence by using DRIFT and ATR/FTIR analytical techniques.

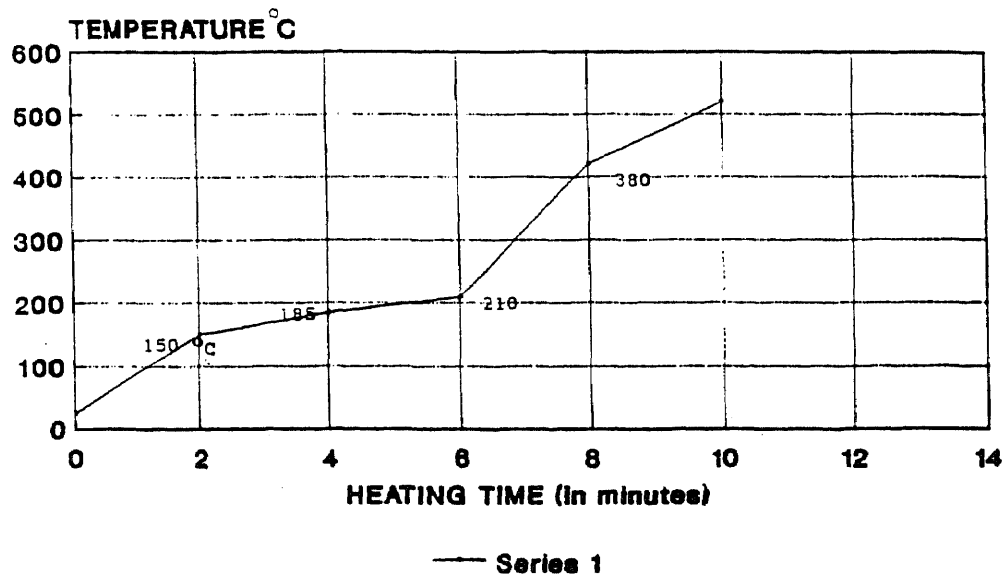
(5) In Figure 6.3 and Figure 6.4, it is observed that there are peaks at about 9 minutes (retention time) in Figure 6.3 and at about 7.5 minutes in Figure 6.4, which are not attributable to anthraquinone. This is evident by comparing the above spectra to the spectrum in Figure 3.2, the spectrum of anthraquinone. So far we do not know which compounds they are or their origin. Mass spectral identification is not sufficient for identification. It is possible, if it were deemed necessary, to obtain infrared spectra by GC/FTIR to make identification more probable.

FIGURE 6.1 C/C₀ IN EXTRACTS FROM CLAY SOIL vs. MICROWAVE HEATING TIME



**EXPERIMENTAL CONDITIONS: SAMPLE SIZE
40 GRAMS, NO WATER ADDED, ULTRASONIC
EXTRACTION.**

**FIGURE 6.2 MICROWAVE HEATING TIME vs.
TEMPERATURE OF CLAY SOIL**



**EXPERIMENTAL CONDITIONS: SAMPLE SIZE
40 GRAMS, NO WATER ADDED, ULTRASONIC
EXTRACTION**

FIGURE 6.3. TOTAL ION CHROMATOGRAM AND MASS SPECTRUM
OF UNKNOWN COMPOUND AT 7.5 min

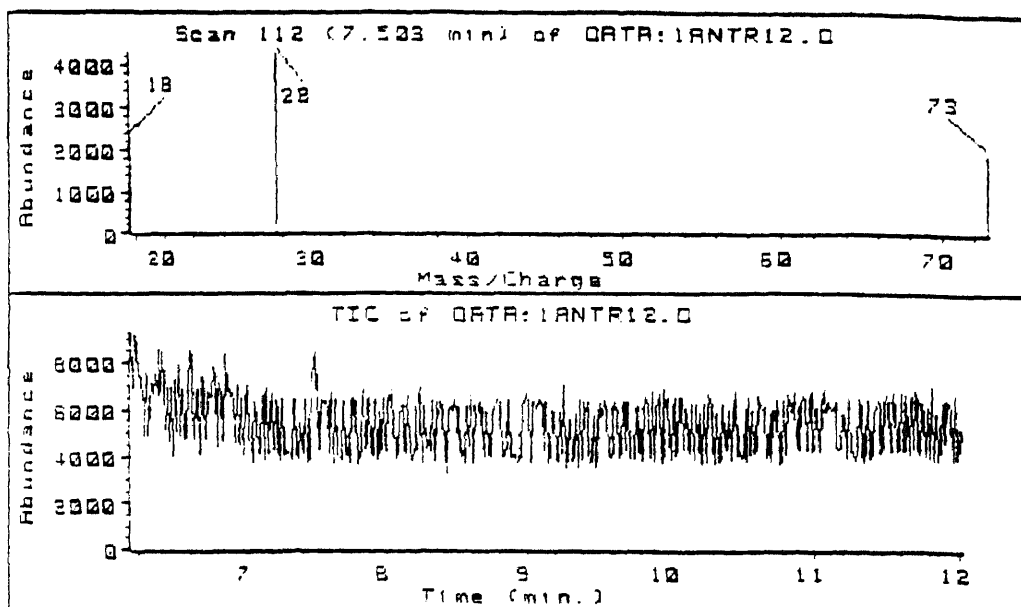
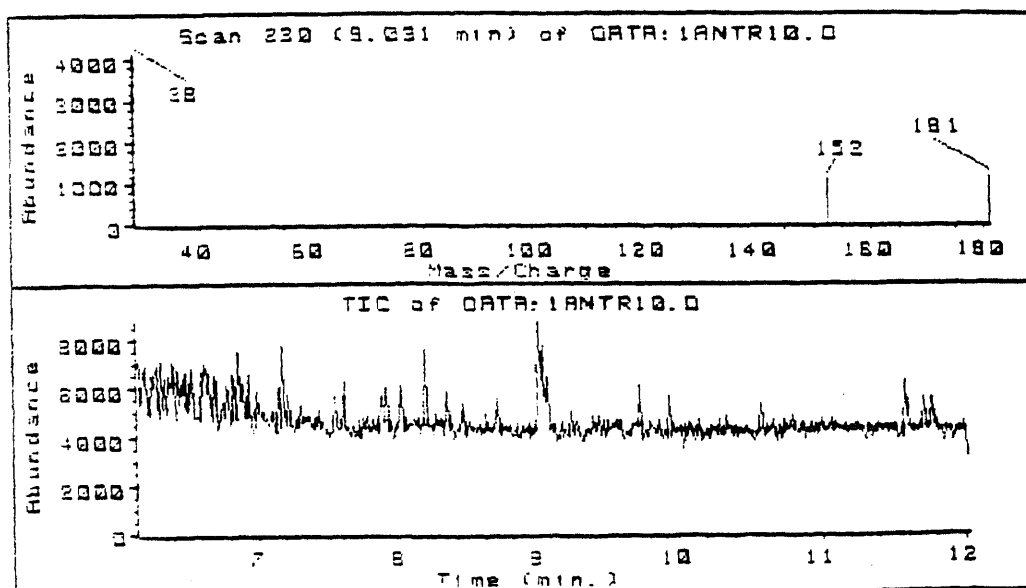


FIGURE 6.4. TOTAL ION CHROMATOGRAM AND MASS SPECTRUM
OF UNKNOWN COMPOUND AT 9.03 min



CHAPTER 7. EXPERIMENTAL SERIES V

THE DETECTION OF ANTHRAQUINONE OR ANY ORGANICS IN EXTRACT FROM CLAY SOIL USING FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

7.1 INTRODUCTION

The objectives of this study were to detect anthraquinone or any organics in the extracts from clay soil treated by microwave energy and obtain the IR spectra of extracts using Fourier Transform Infrared Spectroscopy (FTIR).

An infrared spectrum contains basic information about the composition and structure of a compound. All molecules are made up of atoms linked by chemical bonds and these atoms vibrate with respect to each other. Each molecule has its own specific set of vibration frequencies. The frequencies of these vibrations are not only dependent on the nature of the particular bonds themselves, but are also affected by the entire molecule and its environment. If infrared radiation of a given frequency strikes a sample whose molecules have a same vibrational frequency as that of the incident radiation, and the selection rules are not violated, the molecule absorbs radiant energy, and the energy of the molecule is increased. If the incident frequency differs from the characteristic frequencies of the molecule, the radiation passes through unchanged.

There are numerous types of IR instruments available. For our research, the Digilab FTIR spectrometer (FTS-40) was used.

The basis of any FTIR spectrometer is the Michelson interferometer, which contains one fixed and one movable mirror, and a beamsplitter. The beamsplitter transmits half of the incident radiation to the moving mirror and reflects the other half to the fixed mirror. The two beams, reflected by these mirrors, go back to the beamsplitter, where they recombine. The beams interfere constructively or destructively depending on the position of the moving mirror and the frequency of the radiation. The moving mirror is translated at a constant velocity by a linear motor under computer control. If the position of the movable mirror is such that two beams travel exactly the same distance before reaching the detector (retardation or optical path difference $\sigma = n$ where $n=0,1,2,\dots$), then the two beams are in phase and will reinforce each other (constructive interference). Hence, the energy arriving at the detector will be a maximum. On the other hand, if the position of the movable mirror is such that the optical path length of the two beams is different by $(n+1)\lambda/2$, the two beams are 90° out of phase and will exactly cancel each other out. The resulting energy hitting the detector will be a minimum. Thus, as the movable mirror travels a certain distance, an interferogram (electric signal) will result, where the intensity of the radiation at the detector varies as a cosine function of the optical retardation. While an interferogram contains all the information obtainable by a spectrometer at the given settings, the form of this information is not very useful for chemical analysis. A HeNe laser is used to generate a reference signal which measures the retardation and provides an internal clock. This clock enables the spectrometer electronics to sample the interferogram at precise intervals, generating a digital signal compatible with the computer. The computer converts the interferogram into a single beam spectrum by a set of mathematical operations consisting mainly of a Fourier transform.

7.2 EXPERIMENT

7.2.1 Instrumentation

Digilab FTS-40 Fourier Transform Infrared Spectrometer was used with 3240 SPC data system. A model GRAPHTEC WX 4731 plotwriter and a model OKIDATA, MICROLINE 182 TURBO printer were used in this study. The number of scans chosen was 64 and the resolution was 8 cm^{-1} .

Potassium chloride windows were used with 0.01 mm spacer. Nonpolar liquids will generally require thicker spacers than polar liquids. Also, to observe weak absorption bands, thicker spacers are required.

7.2.2 Experimental samples

The samples of extracts were chosen from Experimental Series IV; the designations of samples and the different experimental conditions are shown in Table 7.1. The concentration of anthraquinone in the extract was detected by GC/MS.

TABLE 7.1

THE DESIGNATIONS AND EXPERIMENTAL CONDITIONS OF EXTRACTS

No.	Designation	Exposure time to MW	Concentration
1	ANTH3TR	solution	2963 ppm
2	AN4BLU2TR	blank	999.6ppm
3	1ANTR4TR	4 min	60.24ppm
4	1ANTR8TR	8 min	0
5	1ANTR10TR	10min	0(45.27)*

* discussed in chapter 6.

7.3 IR SPECTRA

(1) Spectrum of toluene is shown in Figure 7.1.

(2) Spectrum of anthraquinone solution is shown in Figure 7.2.

(3) Spectrum of blank extract, AN4BLU2TR, is shown in Figure 7.4.

(4) Spectra of extracts from clay soil, which were treated by microwave energy 4 minutes, 8 minutes, and 10 minutes respectively, are shown in Figure 7.5, Figure 7.6, and Figure 7.7.

7.4 DISCUSSION AND RECOMMENDATIONS

(1) Figure 7.1 is a typical transmittance spectrum of toluene. It is evident by comparison to the spectrum in Figure 7.3 copied from "The Aldrich Library of Infrared Spectra" by Charles J. Pouchert. In addition to the similarity, it is observed that there were more peaks in Figure 7.1, than in Figure 7.3. This may be due to the higher sensitivity of FTIR or due to some impurities in the toluene. More molecular fine structure can be found in a FTIR spectrum.

(2) In Figure 7.2, a spectrum of anthraquinone solution, the carbonyl band was at 1678 cm^{-1} , which was the same as the comparable band in the blank extract. It was expected because anthraquinone did not react with clay soil directly, that is, it

did not form any detectable new bond in the new environment before being treated with microwave energy.

(3) It was found in the above experiments that no anthraquinone was detected in the extracts after more than 8 minutes of microwave treatment. The detection methods used were GC/MS, FTIR and, also, UV-VIS spectroscopy. Thus, the next step was to focus on the solid sample directly, that is, study the anthraquinone-impregnated clay soil which was treated by microwave energy. Since the sample is a solid the techniques for characterization were ATR/FTIR and DRIFT, respectively. Clay soil is a non-uniform system. To avoid problems associated with the heterogeneity of clay soil, clay minerals, a major component of clay soil, was used as the substrate in the following studies.

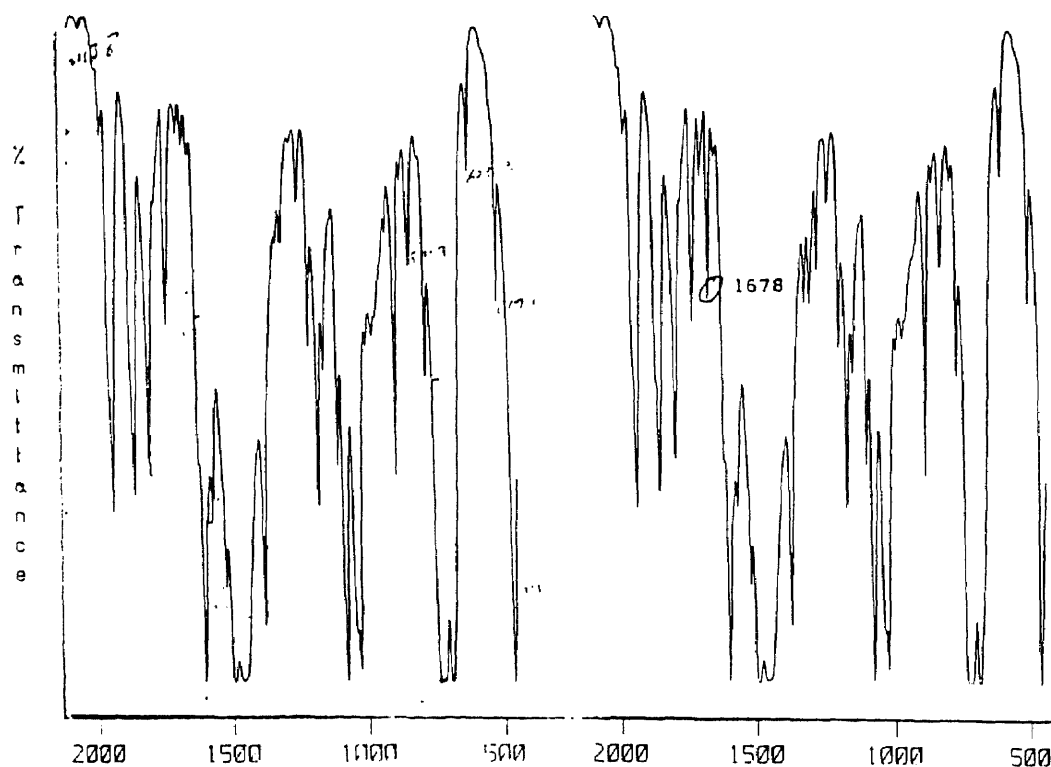
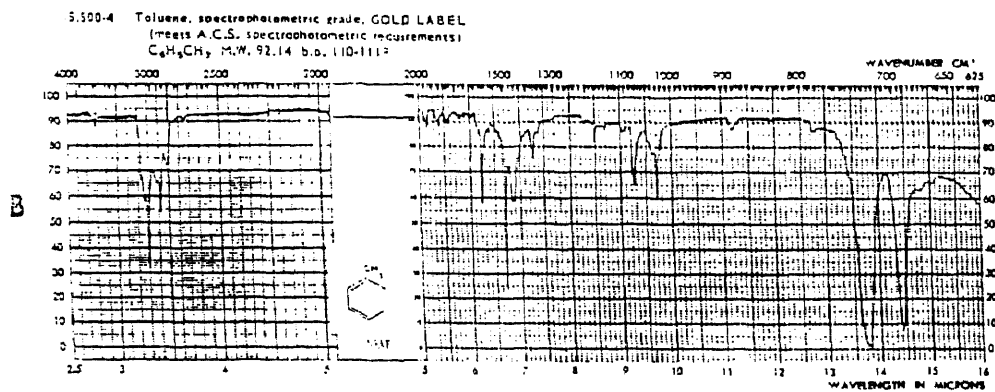


FIGURE 7.1. THE SPECTRUM OF TOLUENE

FIGURE 7.2. THE SPECTRUM OF ANTHRAQUINONE
SOLUTION (2000 ppm)

FIGURE 7.3. THE SPECTRUM OF TOLUENE (COPIED FROM ALDRICH)



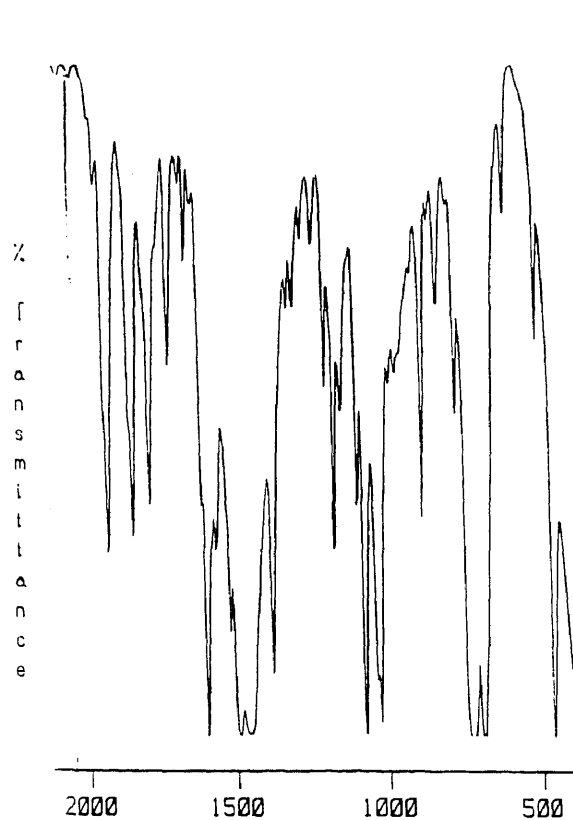


FIGURE 7.4. THE SPECTRUM OF EXTRACT (AN4BLU2TR) FROM CLAY SOIL

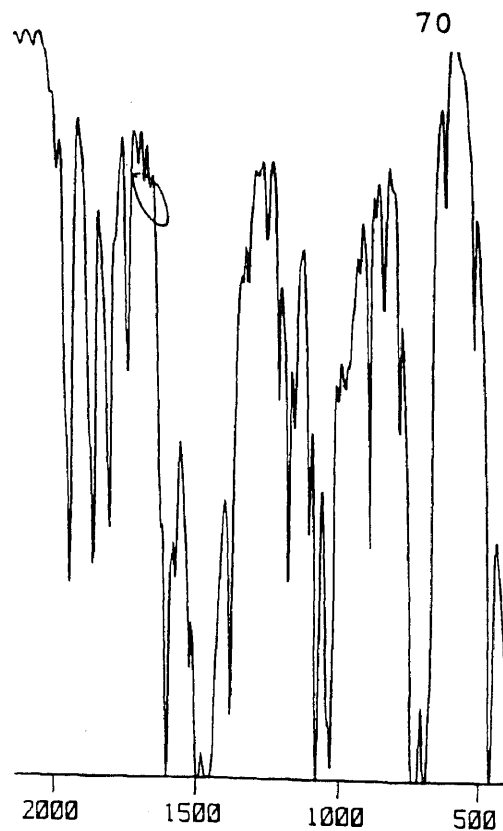


FIGURE 7.5. THE SPECTRUM OF EXTRACT FROM CLAY SOIL (treated by MW 4 min)

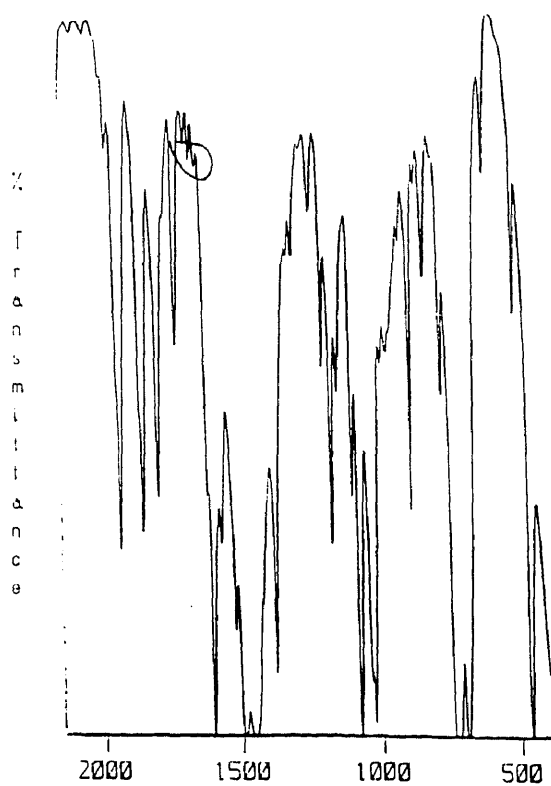


FIGURE 7.6. THE SPECTRUM OF EXTRACT FROM CLAY SOIL (treated by MW 8 min)



FIGURE 7.7. THE SPECTRUM OF EXTRACT FROM CLAY SOIL (treated by MW 10 min)

CHAPTER 8. EXPERIMENTAL SERIES VI

INVESTIGATION OF SORPTION INTERACTIONS BETWEEN ANTHRAQUINONE AND CLAY AFTER MICROWAVE TREATMENT USING DIFFUSE REFLECTANCE FOURIER TRANSFORM INFRARED SPECTROSCOPY (DRIFT)

8.1 INTRODUCTION

The question studied was whether or not microwave treatment leads to the fixation of non-volatile organics on solid substrates. The sorption interactions between anthraquinone and kaolin in the presence of magnetite using diffuse reflectance Fourier transform infrared spectroscopy were investigated.

Until the 1960s, x-ray diffractometry was used almost exclusively to study the structure of the complexes formed between clay and organic compounds. While this method has yielded much useful information on the arrangement and conformation of the organic molecule in the interlayer space of such minerals (MacEwan 1961; Walder 1961; Greenland 1965), its usefulness in investigating changes that may take place in the structure of the adsorbed compound is limited.

The recent development of a solid state sampling / analytic technique, namely, diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) has provided a potential means to observe structural changes on a molecular scale and so provide insights into the nature of the clay-organic bond (Bowen et al. 1989; Porro and Batrachian 1990).

The principle behind the application of DRIFT to the study of the clay-organic system is that many substances in their natural state (e.g., powders and rough surface solids) exhibit diffuse reflection, i.e. incident light is scattered in all direction as opposed to specular reflection where the angle of incidence equals the angle of reflection. Figure 8.1 shows the optical phenomenon which occurs when a focussed beam of infrared radiation impinges on the surface of a fine powder in a sample cup. If the wavelengths of the incident radiation are of similar sizes to that of the particles, a large portion of the radiation undergoes absorption, reflection, and scattering by the sample. This radiation emerges diffusely in all directions, having suffered attenuation at frequencies where the sample absorbs. Large solid angle optics collect this radiation and direct it towards the detector.

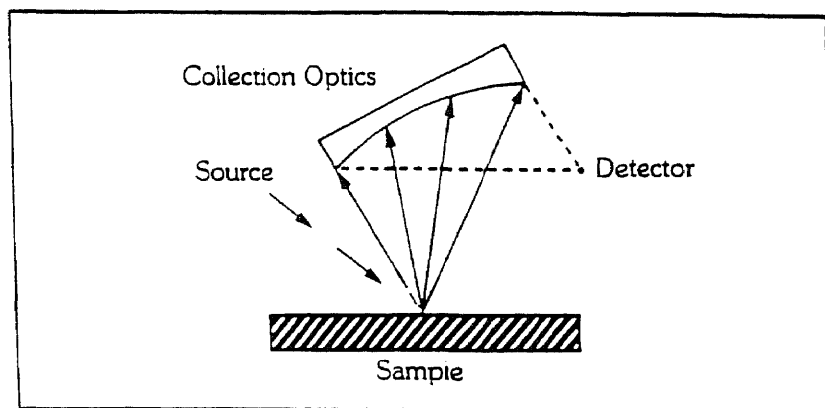


Figure 8.1. In diffuse reflectance, the incident beam undergoes absorption and scattering by the powdered sample and is then collected and focused on the detector.

In practice, diffuse reflection spectra are complex and are strongly dependent upon the conditions under which they are obtained. These spectra can exhibit both absorbance and reflectances due to contributions from transmission, internal and specular reflectance components, as well as scattering phenomena. Diffuse reflectance spectra are further complicated by sample preparation, particle size, sample concentration, and optical geometry effects.

In order to obtain a transmission-like spectrum of strongly absorbing samples, it is necessary to grind and dilute the sample in a nonabsorbent powder such as KBr, KCl, Ge, or Si, respectively, because specular reflection produces inverted bands ("reststrahlen bands") in the diffuse reflectance spectrum which reduce the usefulness of traditional transmission reference spectra. Grinding can reduce the contribution of reflection from large particle faces. Dilution ensures deeper penetration of the incident beam into the mixture, thus increasing the contribution to the spectra of the transmission and internal reflection components.

For quantitative studies, the resultant reflectance spectrum should be converted into Kubelka-Munk (K-M) format, in which the ordinate is directly proportional to concentration. For transmission spectra, the preferred scale is in units of absorbance. For diffuse reflectance, the best approximation is given by transforming the reflectance spectra with the Kubelka-Munk function,

$$f(R) = (1-R)^2 / 2R = 2.303ac / s$$

R = reflectance

a = absorptivity

c = concentration

s = scattering coefficient.

The "s" depends on both the particle size and the degree of sample packing, thus the K-M function can be used for accurate quantitative analysis, provided the particle size and packing method are strictly controlled.

The first and most obvious application of qualitative analysis by DRIFT spectrometry is the rapid identification of a powder without sample preparation. Not only is the sample preparation time very short but the amount of sample required to produce a strong spectrum is also quite small; 100 μ g of most samples is all that is required to give a strong spectrum; bands from less than 200 ng of moderately absorbing compounds can usually be observed (Fuller and Griffiths 1979; Krishnan, Hill, and Brown 1980).

In the light of the abovestated advantages, DRIFT was chosen to investigate the sorption interaction between anthraquinone and clay in this study.

8.2 EXPERIMENT

8.2.1 Instrumentation

A model FTS-40 Fourier Transform Infrared Spectrometer (Digilab) was used in recording the spectra presented in this thesis. The diffuse reflectance measurements were performed using the diffuse reflectance accessory designed exclusively for Bio-Rad FTSTM Spectrometers. The powder samples were held in stainless steel cups, 10 mm in diameter and 1 mm deep.

A model Sharp, #Carousel II microwave oven and a muffle furnace (Type 10500) were used to treat samples.

8.2.2 Materials

The solid state FTIR substrate, potassium bromide (KBr), was high purity spectroscopic grade obtained from a commercial vendor and subsequently stored in a vacuum chamber with a desiccant.

The clays, namely, Kaolin (KGa-1), Ca-Montmorillonite (SAz-1 and STx-1), Attapulgite (PFI-1), and Barasym SSm-100 (SYN-1) were obtained from the Clay Minerals Society Repository, University of Missouri, Department of Geology.

The properties of the Kaolin clay are as follows (Olphen and Fripiat 1979):

KGa-1 Kaolinite (well crystallized)

a) Chemical Composition (%):

SiO ₂ : 44.2	Al ₂ O ₃ : 39.7	TiO ₂ : 1.39	Fe ₂ O ₃ : 0.13
FeO: 0.08	MnO: 0.002	MgO: 0.03	CaO: n.d.
Na ₂ O: 0.013	K ₂ O: 0.050	F: 0.013	P ₂ O ₅ : 0.034
Loss on heating: -550 ⁰ C: 12.6; 550-1000 ⁰ C: 1.18			

b) Cation exchange capacity: 2.0 meq/100g

c) Surface area: N₂ area: 10.05 ± 0.02 m²/g

d) Thermal analysis: DTA: endotherm at 630°C , exotherm at 1015°C ; TG: dehydroxylation weight loss 13.11% (theory 14%) indicating less than 7% impurities.

e) Infrared spectroscopy: Typical spectrum for well crystallized kaolinite, however not as well crystallized as a typical China Clay from Cornwall, as judged from the intensity of the 3669 cm^{-1} band. Splitting of the 1100 cm^{-1} band is due to the presence of coarse crystals.

Magnetite- $\text{Fe}^{+2}\text{Fe}^{+3}\text{O}_4$ (Spinel Group), obtained from Ward's natural science establishment, INC., has following properties:

a) Crystallography: Isometric; $4/m\bar{3}2/m$. Frequently in octahedral crystals; rarely dodecahedral. Commonly coarse-to fine-grained granular, massive.

b) Physical properties: Cleavage: None. Commonly shows distinct parting on $\{111\}$. Fracture subconchoidal to uneven; brittle. H.6.0. G. 5.18. Luster: Splendent to dull metallic. Color: Iron-black; opaque. Streak: Black.

c) Composition/Features: A common iron oxide characterized by its strong magnetism, black color, and hardness. Slowly soluble in HCL. Infusible. Strongly magnetic varieties, which act as nature magnets, are known as lodestone.

Magnetite particles of less than $250\mu\text{m}$ in diameter were used. First, the magnetite was crushed, then, sieved.

The anthraquinone and toluene used in this study were described previously.

8.2.3 Experimental procedure

Step 1. Five (5) kinds of clays were scanned by DRIFT to collect comparative spectra. The purpose was to find clays which have no absorption bands in infrared spectra from

1600-1750 cm^{-1} , that is, where carbonyl groups of anthraquinone in the new environment may absorb. The designations of the spectra of the respective clays are shown in Table 8.1.

TABLE 8.1. THE DESIGNATIONS OF SPECTRA OF CLAYS

No.	Clay	Spectra
1.	SAZ-1 Ca-Montmorillonite (cheto)	SAZB1K
2.	STx-1 Ca-Montmorillonite	STXB1K
3.	PFI-1 Attapulgite	PFTB1K
4.	KGa-1 Kaolin	KGAB1
5.	SYN-1 Barasym SSm-100	SYNB1K

Step 2. Clays which absorb in the 1750 cm^{-1} to 1600 cm^{-1} band may overlap carbonyl bands of anthraquinone in some special environments. To remove such overlapping bands, clays were heated in the muffle furnace for 6 hours at 800⁰ C.

Step 3. The microwave absorption of the kaolin clays was studied by measuring the temperature of samples by thermocouples. The samples of kaolin clays were treated in the microwave oven for 2 min, 4 min, 6 min, 8 min, 10 min, 15 min, 20 min, and 30 min, respectively.

Step 4. The microwave absorption of mixtures of kaolin and magnetite powder [ratio (by weight) 50 : 2] was studied by measuring the temperature of samples by thermocouples. The samples of clay and magnetite were treated in the microwave oven for 10 min, 20 min, and 30 min, respectively.

Step 5. The spectrum of neat anthraquinone was collected by DRIFT.

Step 6. The spectrum of anthraquinone-impregnated kaolin was obtained on samples prepared as follows: a 50 ml solution of anthraquinone in toluene (1180 ppm in toluene) was mixed into 50 gram kaolin clay (KGa-1); the sample was placed in a hood for four days to effect the evaporation of the solvent, toluene. The sample, scanned by DRIFT, is designated as the experimental blank (AKGA1).

Step 7. A spectrum of the mixture of anthraquinone, kaolin, and magnetite was collected on a sample prepared by mixing 2 grams of magnetite powder into 50 grams of the kaolin-anthraquinone sample described above. This mixture, scanned by DRIFT, is designated as the experimental blank (AKGAM1).

Step 8. Samples of clay mixed with anthraquinone and magnetite, of the same ratio and preparation as described in step 7 above, were treated in microwave oven 20 min, 25 min, and 30 min. The treated samples were scanned using DRIFT.

The diffuse reflectance data were collected at 4 cm^{-1} resolution for 128 scans, using potassium bromide powder as the background and diluent (The samples

were diluted to approximately 5-10% by weight in KBr and referenced to neat KBr).

8.3. EXPERIMENTAL DATA AND RESULTS

(1) The temperature of kaolin clay after microwave oven treatment is listed in the Table 8.2.

TABLE 8.2.

THE TEMPERATURE OF KAOLIN CLAY AFTER MW OVEN TREATMENT

Treatment time	Temperature $^{\circ}\text{C}$	Treatment time	Temperature $^{\circ}\text{C}$
2 min	50	10 min	150
4 min	80	20 min	200
6 min	100	30 min	200
8 min	130	40 min	200

(2) The temperature of the mixture of kaolin clay and magnetite after microwave oven treatment is listed in the Table 8.3.

TABLE 8.3. THE TEMPERATURE OF THE MIXTURE OF KAOLIN CLAY AND
MAGNETITE AFTER MW TREATMENT

No.	Treatment time	Temperature
1	10 min	200 - 230 $^{\circ}\text{C}$
2	20 min	250 - 270 $^{\circ}\text{C}$
3	25 min	280 - 320 $^{\circ}\text{C}$
3	30 min	400 - 420 $^{\circ}\text{C}$

(3) The temperature of the mixture of anthraquinone-impregnated kaolin with magnetite after microwave energy treatment is listed in the Table 8.4.

TABLE 8.4. THE TEMPERATURE OF THE MIXTURE OF ANTHRAQUINONE, KAOLIN, AND MAGNETITE AFTER MW TREATMENT

No	Designation	Treatment time	Temperature
1	AKGAMH1K	20 min	200 - 230 °C
2	AKGAMH2K	25 min	230 - 260 °C
3	AKGAMH3K	30 min	270 - 290 °C
4	AKGAMH4K	40 min	about 800 °C (adde 6g magnetite)

(4) The infrared spectra obtained from a variety of samples presented in this thesis are as follows:

The spectra of different kinds of clays are shown in Figure 8.2a, Figure 8.3, Figure 8.4, Figure 8.5, and Figure 8.6.

The spectra of clays STx-1 heated by furnace are shown in Figure 8.7.

The spectrum of neat anthraquinone is shown in Figure 8.8.

The spectrum of anthraquinone-impregnated kaolin clay is shown in Figure 8.2b.

The spectrum of the mixture of anthraquinone-impregnated kaolin clay and magnetite (blank) is shown in Figure 8.9a and Figure 8.10a.

The spectrum of the mixture of anthraquinone-impregnated kaolin clay and magnetite which was treated by microwave oven is shown in Figure 8.9b and Figure 8.10b.

The spectra of the mixture of anthraquinone-impregnated kaolin clay and magnetite treated by microwave energy 25 minutes and 30 minutes are shown in Figure 8.11 and Figure 12.

8.4 DISCUSSION AND CONCLUSIONS

(1) Clay is a relatively poor microwave energy absorber. In Table 8.2, it is shown that the temperature of kaolin clay did not increase even when the heating time was more than 40 min. In the experiment, the temperature of clay could reach maximally 200 °C, which might be due to the effect of a glass beaker (all samples were put in the beakers in the sand bath during microwave treatment). When the glass beaker, filled with sand, was treated by microwave oven 20 min, the temperature of the glass beaker reached 170 °C. Meanwhile, the temperature of kaolin was 200 °C during microwave treatment. The difference in temperature may be due to the following reason: the glass beaker heated by microwave oven increased the temperature of the environment, which further increased the microwave absorption ability of the kaolin clay.

Based on this result, 2 grams magnetite (a strong microwave absorber) powder were added to the mixture of anthraquinone-impregnated clay to increase the temperature of the system.

(2) The diameter of magnetite particle used in this study is less than $250\mu\text{m}$. Larger particles were found to agglomerate after microwave treatment; smaller particles did not absorb microwave radiation strongly. Unlike the clays which come in a fine powder state, the magnetite is in the form of a large rock. Several factors must be considered in deciding upon the size of the particles to be used in the experiment following crushing and sieving. Since this mineral has been chosen to act as the heat sink, for strong absorption, it should obey the following relationship: $\lambda = 4\pi a$ (Osepchuk 1975). This equation applies to each component of the system. On the other hand, that relationship leads to the use of particle sizes so large that it is not possible to obtain good spectra. It is necessary to carry out optimization studies to determine the most suitable size.

(3) Table 8.3 shows how the temperature of a mixture of kaolin and magnetite changed during different microwave heating times. When the heating time was 20 min, the temperature reached 250°C to 270°C ; when the heating time was 25 min, the temperature reached was 280°C to 320°C . Previous studies showed that there was no detectable anthraquinone in the clay soil extract when the microwave treating time was over 8 min for which the corresponding temperature was over 380°C . Based on those studies, treatment times of 20 min, 25 min, and 30 minutes, respectively, were chosen initially in this study.

(4) Comparing Table 8.3 and 8.4, it is found that the temperature of the sample of the mixture of clay, anthraquinone, and magnetite was lower when anthraquinone was present in the sample than otherwise. This indicates that the system might absorb energy to form new bonds during microwave treatment: the absorption of the energy results in a relatively lower sample temperature compared with the mixture of clay and magnetite.

(5) Figure 8.3, Figure 8.4, Figure 8.5, and Figure 8.6 show that SYN-1, STx-1, SAz-1, and PFi-1 all have a strong band in the 1700 cm^{-1} - 1600 cm^{-1} region, which may affect the result of this study, that is, may overlap the carbonyl stretching band of a complex of anthraquinone-clay if it were to exist. The existence of such bands in clays may be due to hydration and HOH bond deformations. Initially it was thought that those clays could be used as substrates in our research after pretreatment in the muffler furnace at 800°C for 6 hours to remove those interfering peaks (see Figure 8.7). However, it was subsequently found, in results to be discussed presently, that those clays can be used as substrata directly because the magnitude of the carbonyl group shift is just approximately 17 cm^{-1} .

(6) Figure 8.2a is the spectrum of kaolin clay used in this study, which shows that there was no absorption between 1600 cm^{-1} and 1700 cm^{-1} . For that reason kaolin clay was chosen to be the first substrate studied.

(7) From the spectra of pure anthraquinone and anthraquinone-impregnated kaolin clay, it is observed that there is almost no peak shift in the carbonyl band compared to its spectra in solvents, diluents, and mulls (see Table 8.5). It is inferred that anthraquinone adsorbs weakly on kaolin.

TABLE 8.5. CARBONYL BAND OF ANTHRAQUINONE IN DIFFERENT SOLVENT OR DILUENT

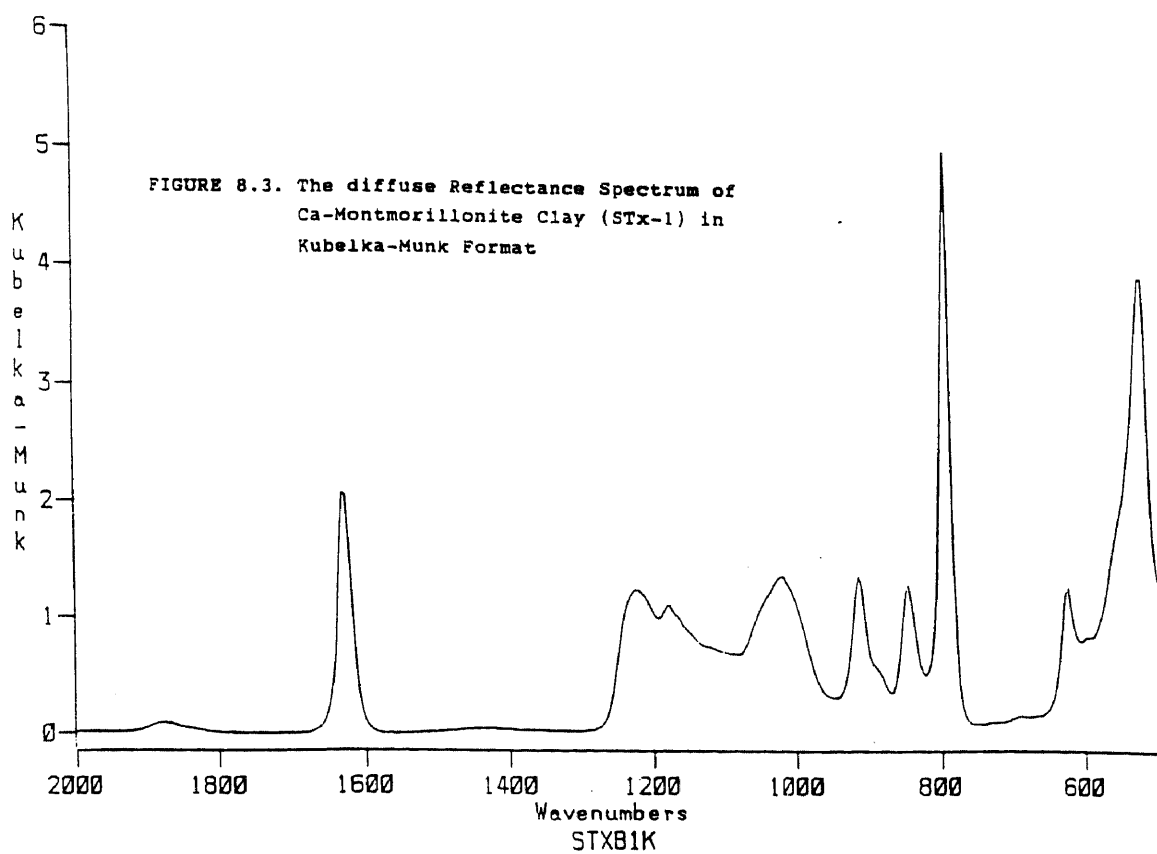
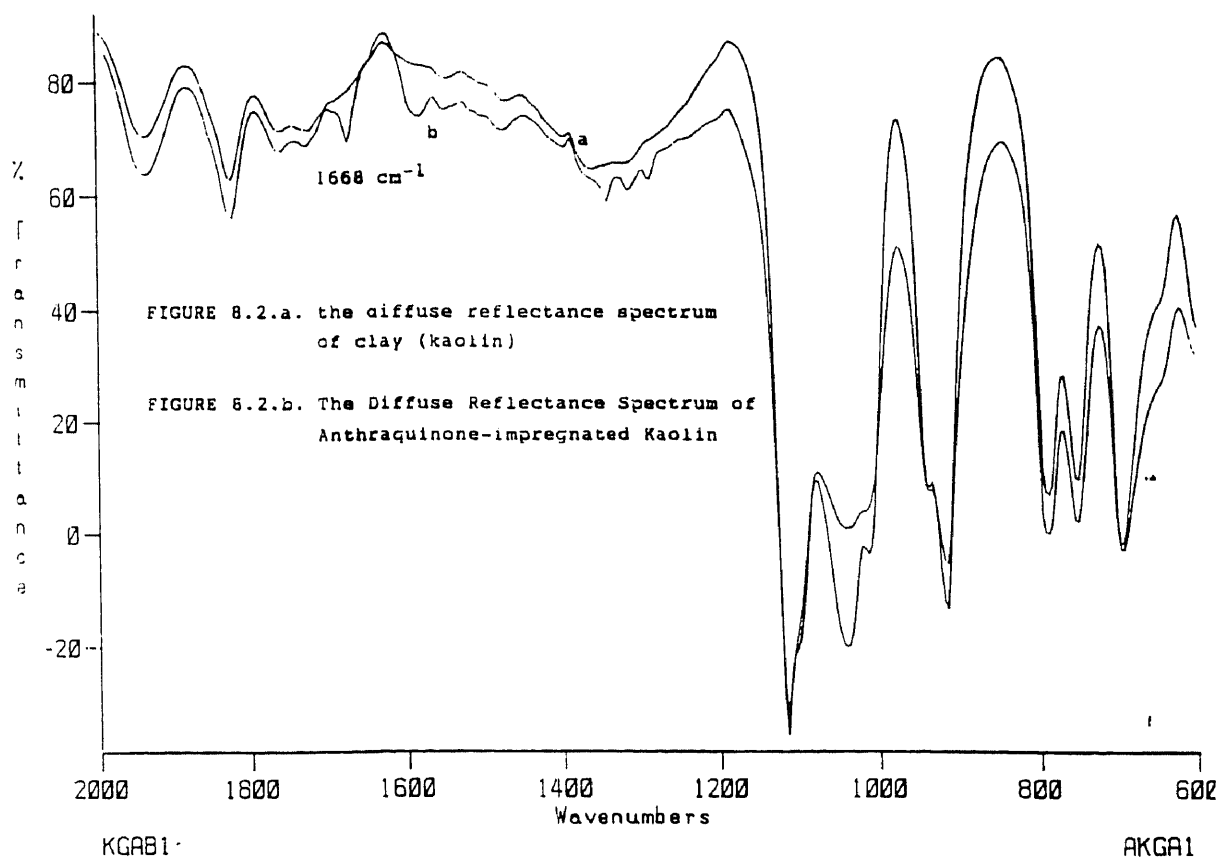
Solvent (diluent)	frequency of c=o band	Spectrum
KBr	1668 cm ⁻¹	Fig.8.8 (DRIFT)
Kaolin clay	1668 cm ⁻¹	Fig.8.2a(DRIFT)
CCL ₄	1680 cm ⁻¹	Fig.8.13(FTIR)
CH ₃ CL	1675 cm ⁻¹	Fig.8.14(FTIR)
CS ₂	1676 cm ⁻¹	Fig.8.115(FTIR)
Toluene	1678 cm ⁻¹	Fig.7.3 (FTIR)
Nujol mull	1675 cm ⁻¹	(Adrish)

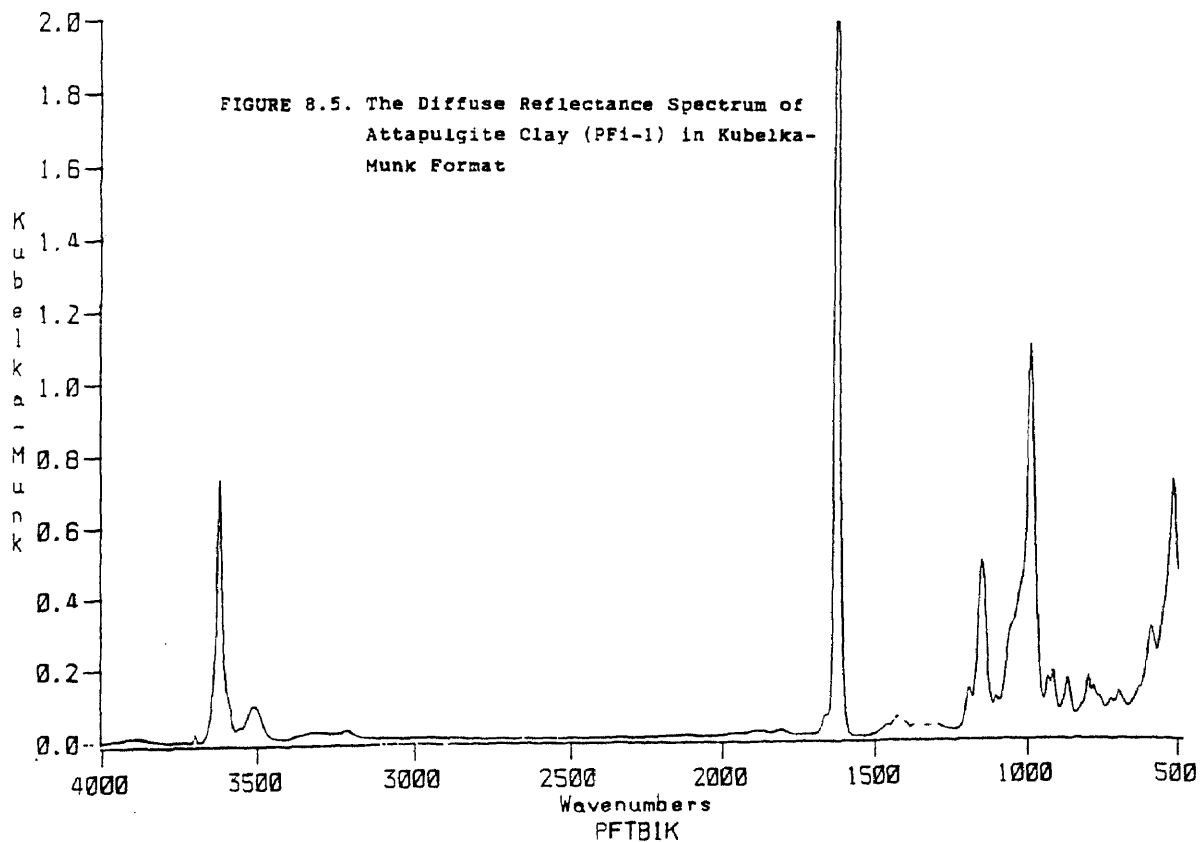
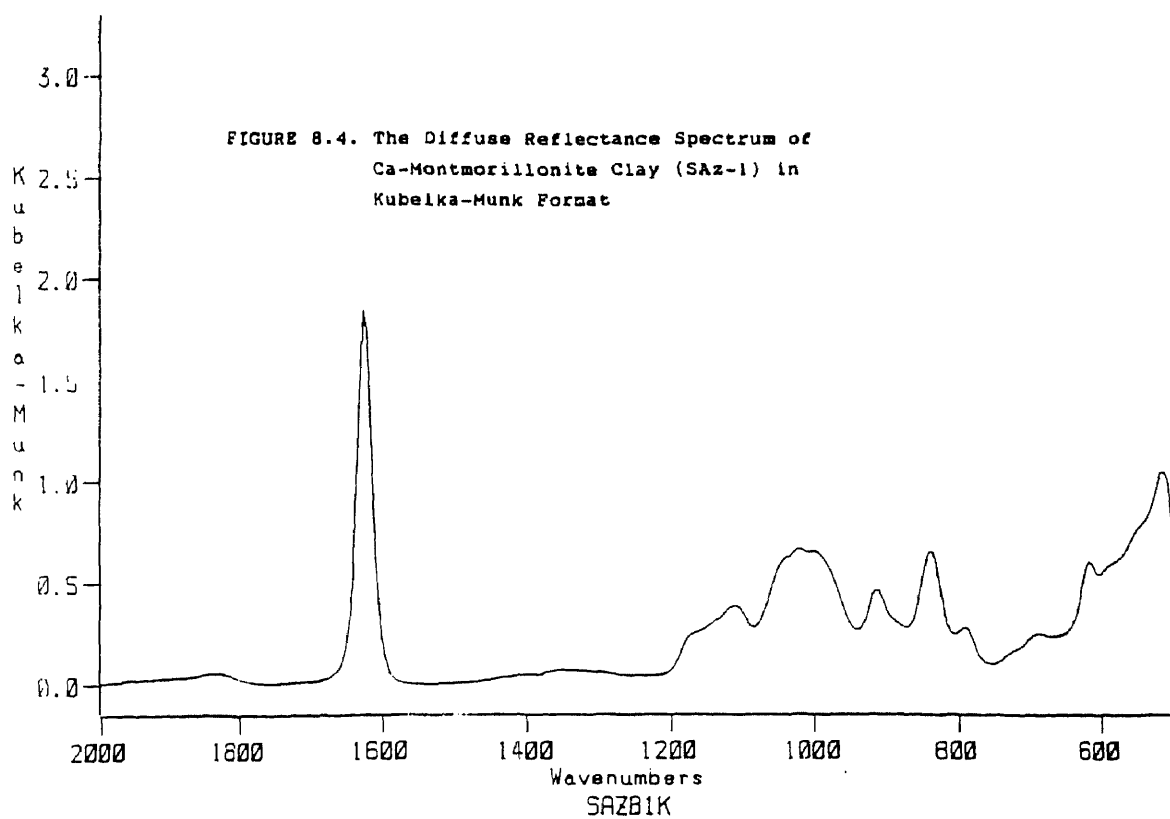
(8) The spectra of the samples of anthraquinone-impregnated kaolin clay before and after microwave energy treatment were compared. From the overlap shown in Figure 8.9 and Figure 8.10 which was expanded from Figure 8.9 in the K-M form, a significant upfield spectrum shift of 17 cm⁻¹ is observed in the carbonyl absorption band region. The c=o band shifts 17 cm⁻¹ from 1668 cm⁻¹ to 1685 cm⁻¹ when microwave treatment takes place in the presence of magnetite. It is also found some new bands were formed. The same band shift and formation also can be observed in Figure 11 and Figure 12 corresponding to heating times of 25 minutes and 30 minutes, respectively. The upfield shift to higher frequency is indicative of stronger bonding. It is suggested that the adsorption of anthraquinone on kaolin may be brought about by microwave heating of the magnetite.

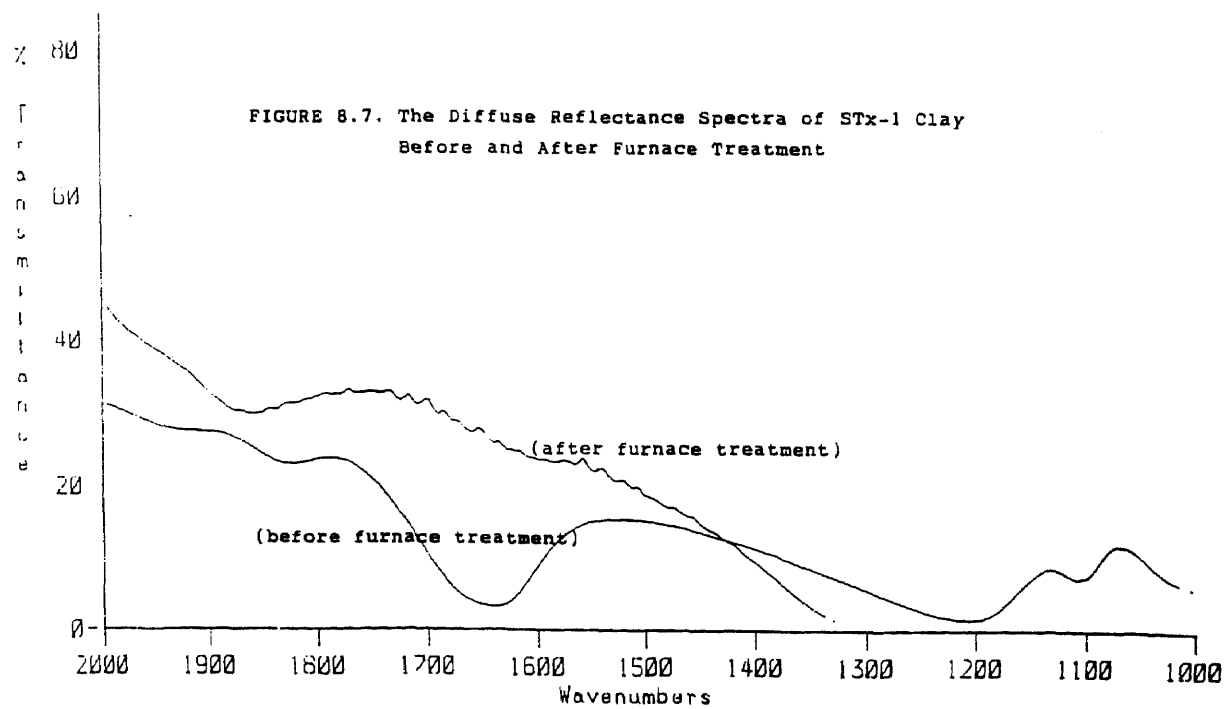
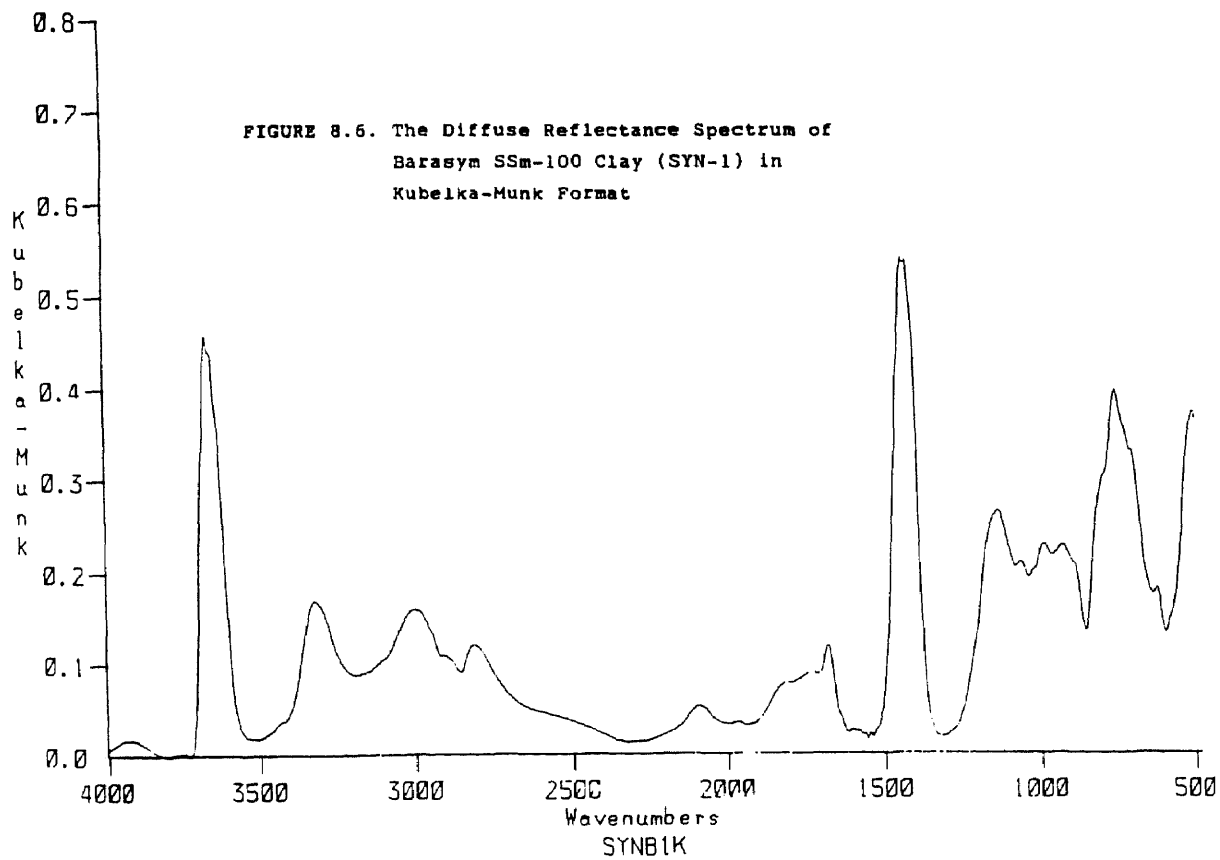
(9) From the aforecited figures, it is also observed that there are two carbonyl bands: one in 1668 cm⁻¹ and the other in 1685 cm⁻¹. Anthraquinone is a highly symmetrical compound whose two carbonyl groups are in the same environment,

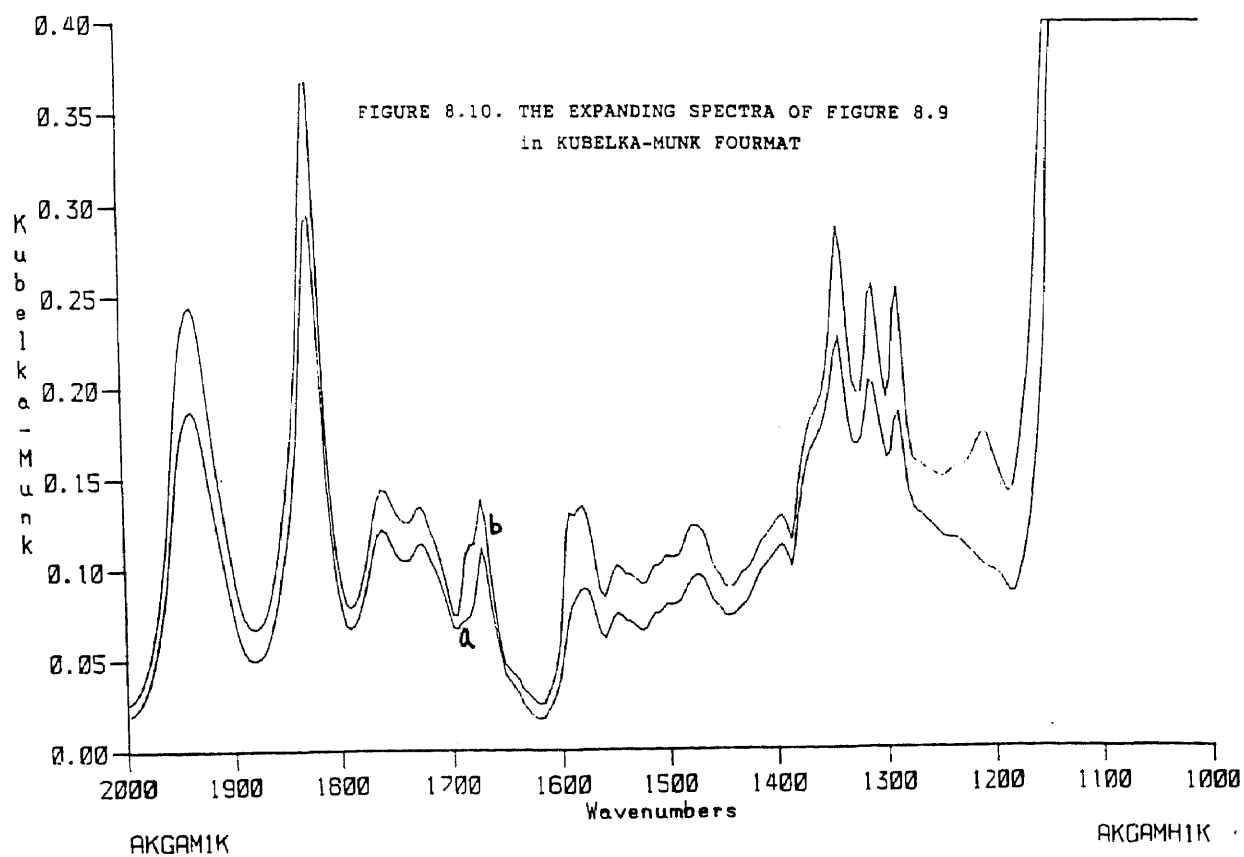
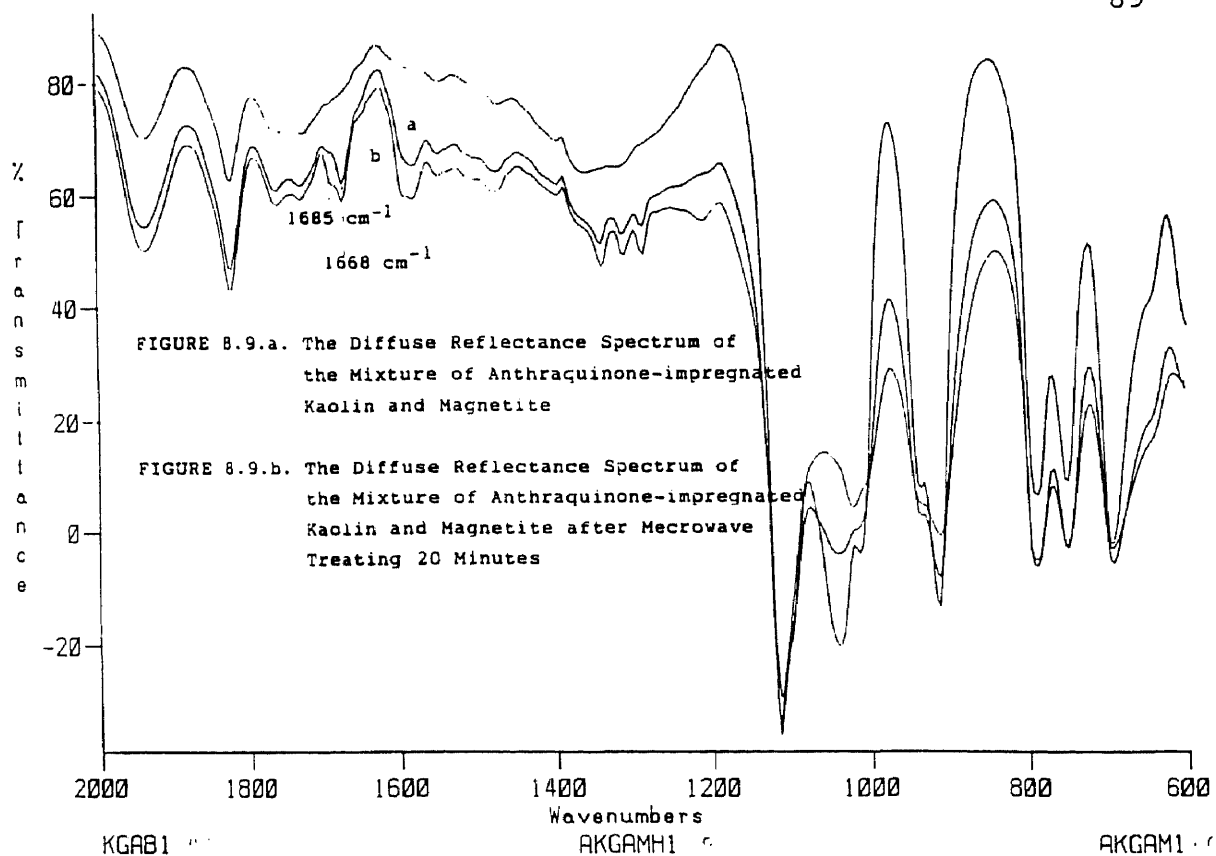
resulting in just one IR absorbing band. Now, after microwave energy treatment, two carbonyl bands were found. This fact indicates that one carbonyl group in the anthraquinone remains unchanged, while the other one may interact with clay. Besides, a residue band (1668 cm^{-1}) also can exist because of some trace anthraquinone. In this study, when the treatment time was 30 min, the corresponding temperature was about 290°C . Recall that in the previous study, when the temperature reached more than 380°C , no extractable anthraquinone could be found. It is suggested that next study be carried out with a little longer treatment time to see if those two carbonyl bands will still exist together or not.

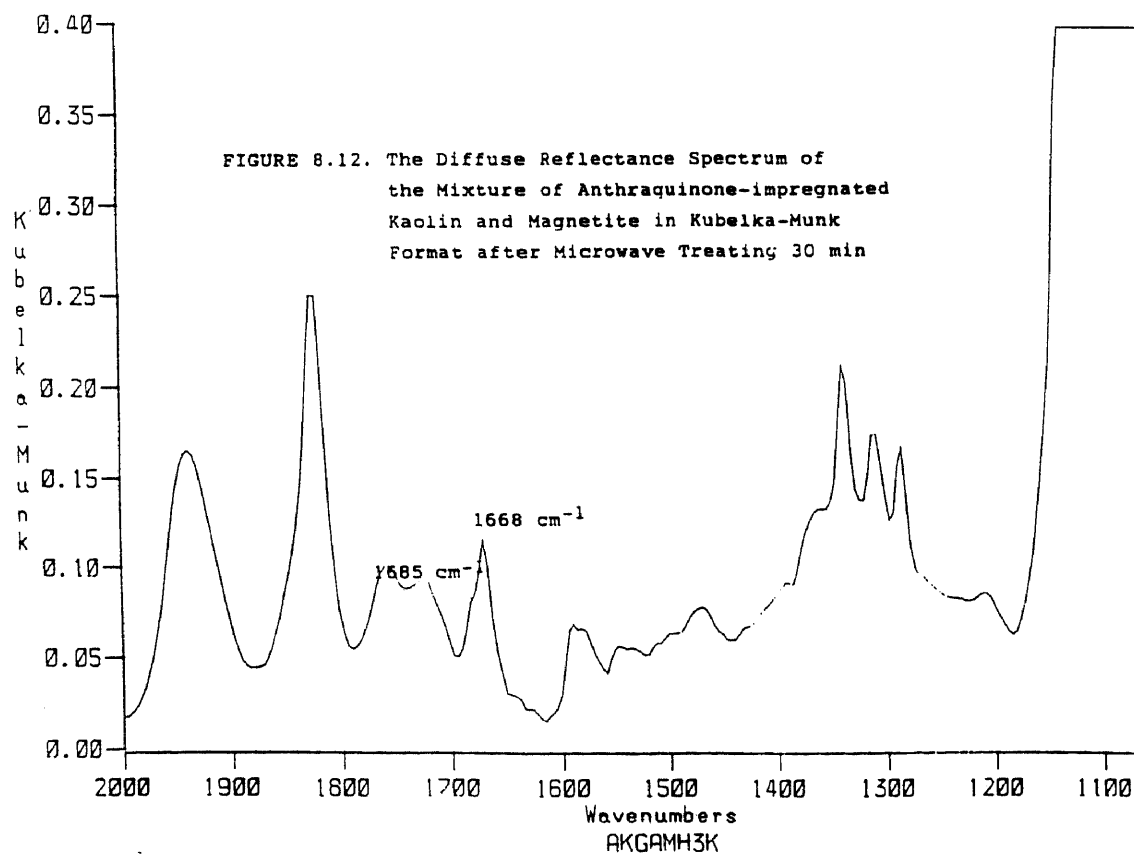
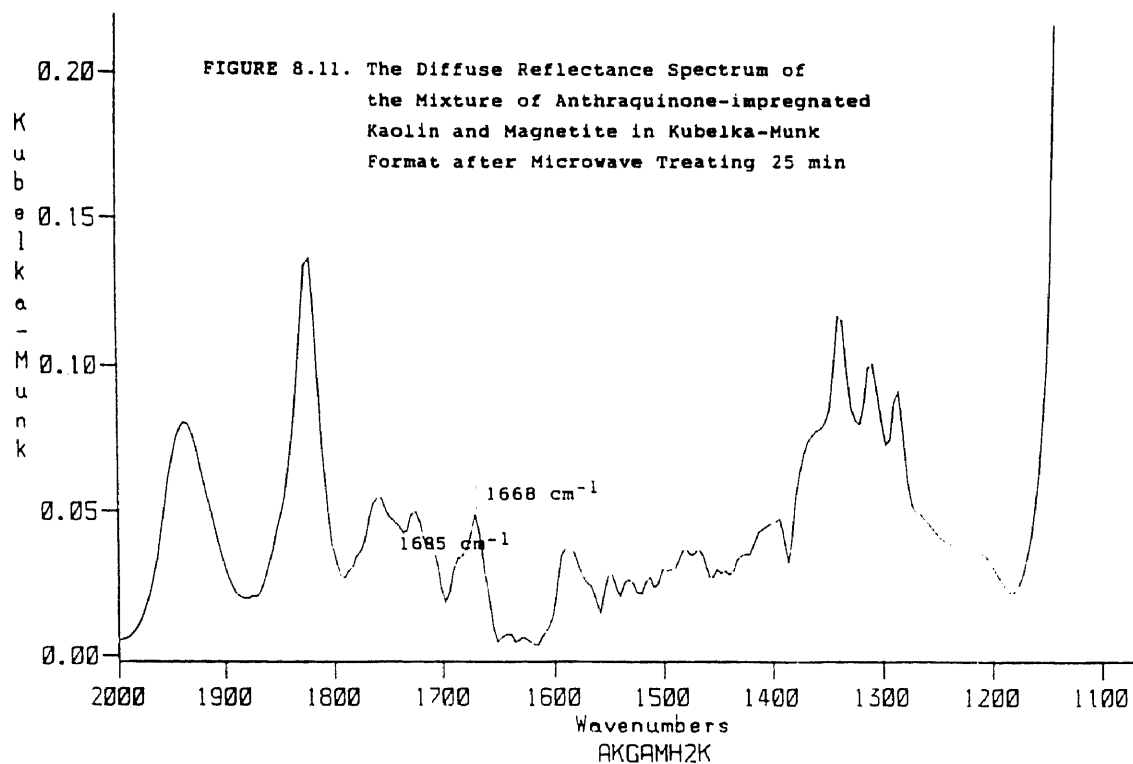
(10) The results of this study raise the following questions: Will heat alone be effective or is the microwave heating of the magnetite critical? Will higher temperatures strengthen the adsorption or chemical changes? In future studies, the effect of thermal heating up to about the same temperature as that reached in microwave heating, in steps up to 600°C , will be carried out. It is also suggested that a comparative extractability study be carried out to see if the anthraquinone, in the samples in which there has been inferred that adsorption has occurred, becomes more difficult to extract.

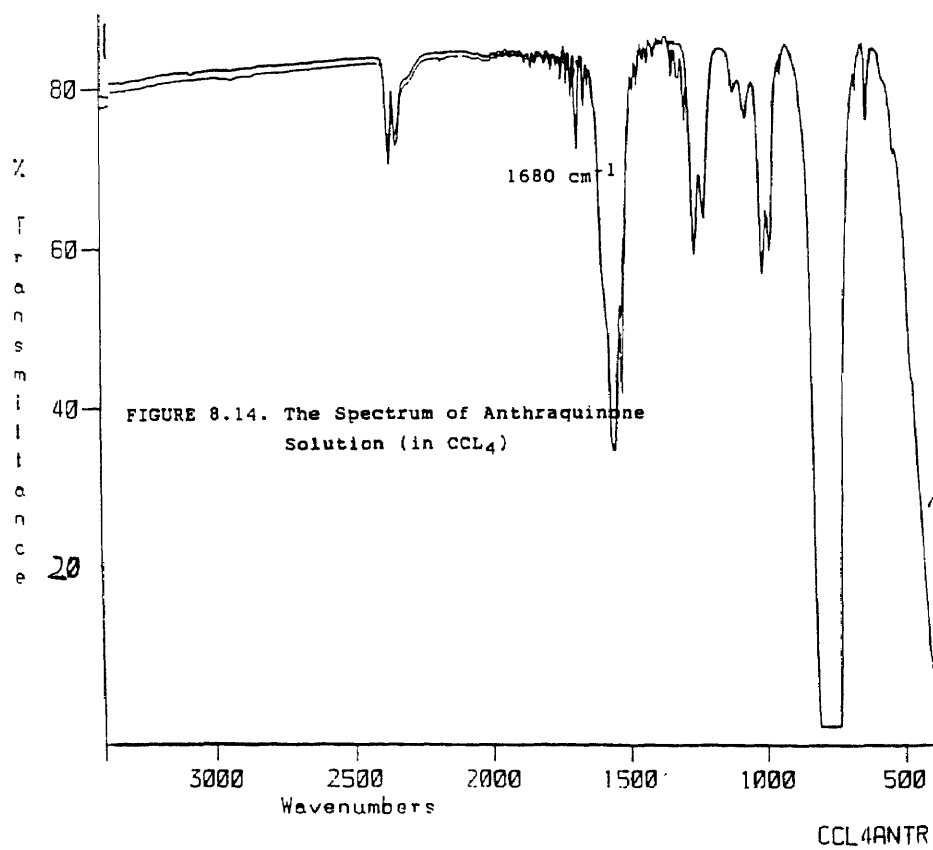
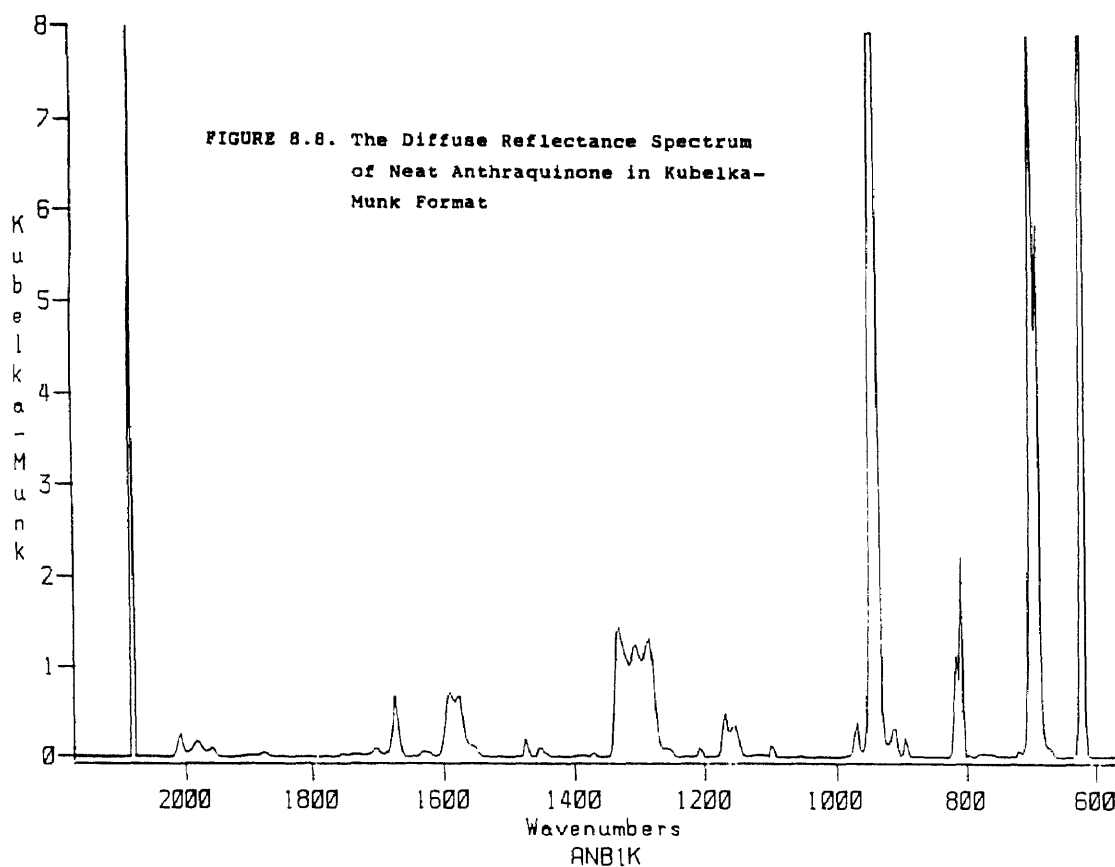


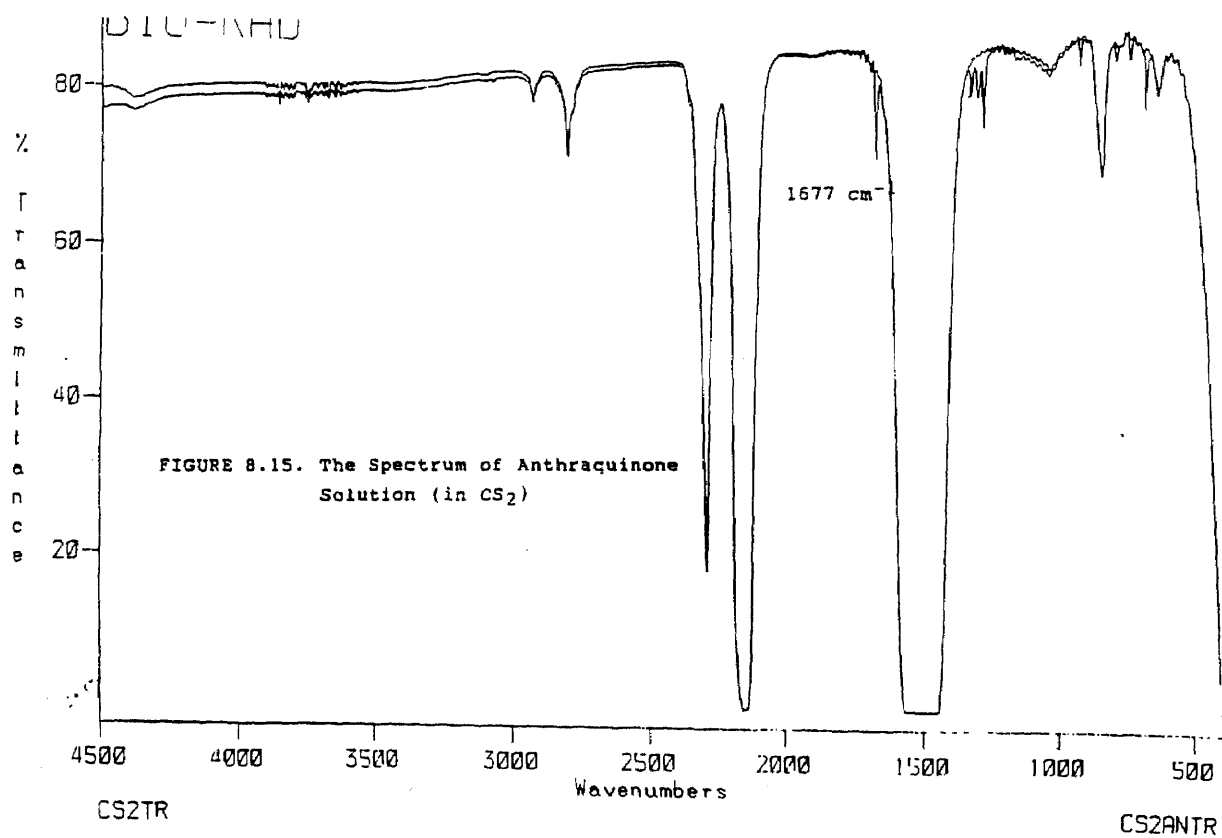
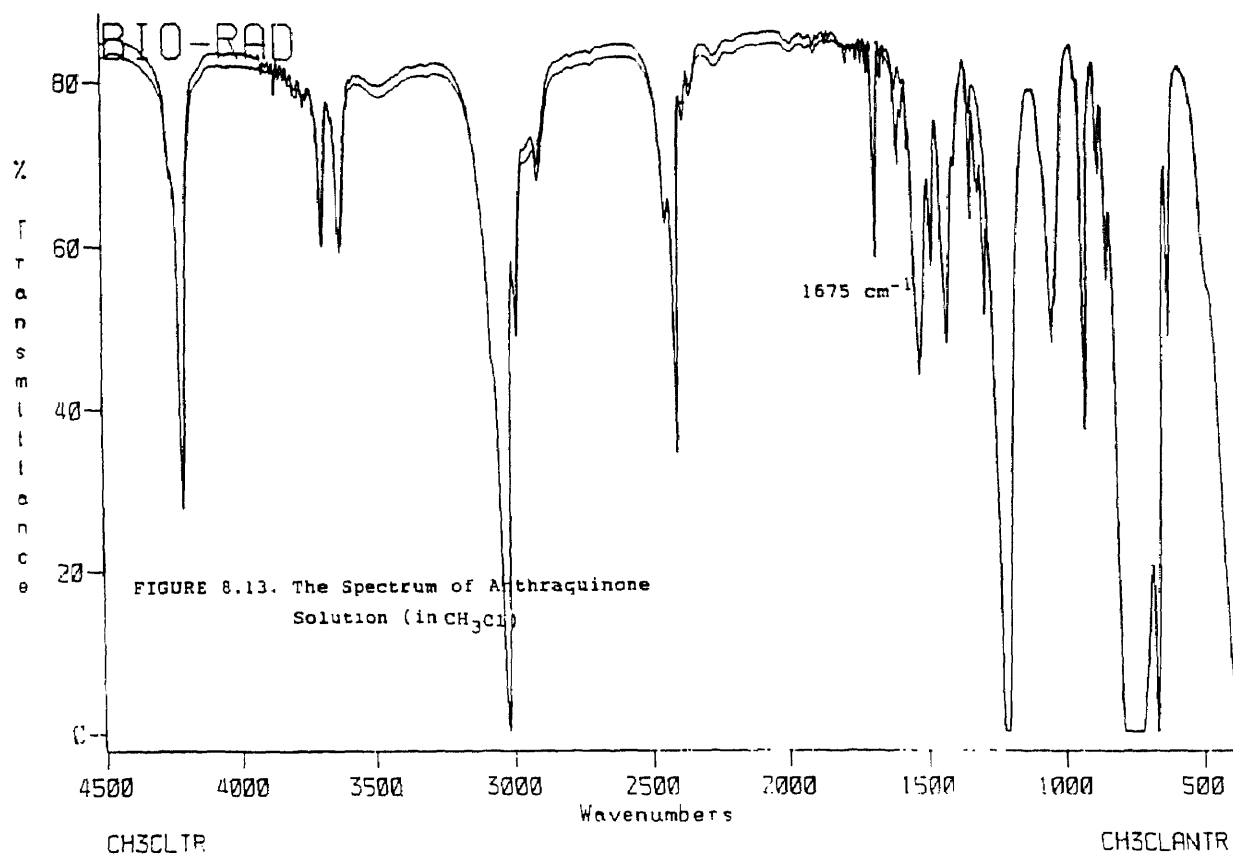












CHAPTER 9. EXPERIMENTAL SERIES VII

THE USE OF HORIZONTAL ATTENUATED TOTAL REFLECTANCE FTIR FOR THE STUDY OF SORPTION INTERACTIONS BETWEEN ANTHRAQUINONE AND CLAY AFTER MICROWAVE TREATMENT

9.1 INTRODUCTION

Horizontal ATR is a variant of solid ATR which is also referred to as internal reflectance spectroscopy (IRS). In ATR, a material is pressed against a special crystal (IRE) composed of a material with a high index of refraction, such as ZnSe, KRS-5, Si, or Ge. When the angle of incidence of the infrared radiation at the sample-IRE interface is greater than or equal to the critical angle, total internal reflectance occurs. The critical angle is dictated by Snell's law, which takes into account the refractive index of both the sample and the IRE. The apex of the angle of reflection lies several wavelengths outside of the face of the crystal. Thus a material placed on the crystal surface can absorb infrared radiation. The incident radiation exiting the crystal will contain absorption bands characteristic of the material on the surface of the crystal. When this spectrum is ratioed against a background spectrum taken through the crystal without a sample present, a spectrum very similar to a transmission spectrum is obtained. Internal reflectance techniques are typically used for sampling strongly absorbing materials or studying surfaces. In the "Horizontal ATR Accessory Manual" (091-0507), it is said that the Bio-Rad Horizontal ATR accessory has been designed for fast, simple, and reproducible analyses of a broad range of samples which include powders, pastes, gels, semi-solids, films, opaque materials, and liquids. Our samples are powders and, also, clay is a strong absorbant material. In this study, therefore,

the practical applicability of ATR/FTIR to the study of the sorption interaction between anthraquinone and clay effected by microwave energy treatment was investigated in a cursory manner.

9.2 EXPERIMENT

9.2.1 Instrumentation

A Digilab FTS-40 FTIR with Bio-Rad Horizontal ATR accessory including a 45° 84 X 9 X 6 mm ZnSe crystal was used in this study. The resolution was 4 cm⁻¹; scans, 64; detector, DTGS.

9.2.2 Procedure

Step 1: A single beam spectrum was collected as the background, with nothing against the IRE crystal face.

Step 2: A 3 inch long piece of a adhesive tape was cut, and the sticky surface placed against the IRE's surface. A reflectance spectrum of the tape was collected and compared with one listed in the "Horizontal ATR Accessory Manual" to check instrumental operation conditions and procedures.

Step 3: Reflectance spectrum of kaolin clay were collected to see if the ATR/FTIR technique could possibly be used for our research purpose.

9.3 EXPERIMENTAL RESULTS

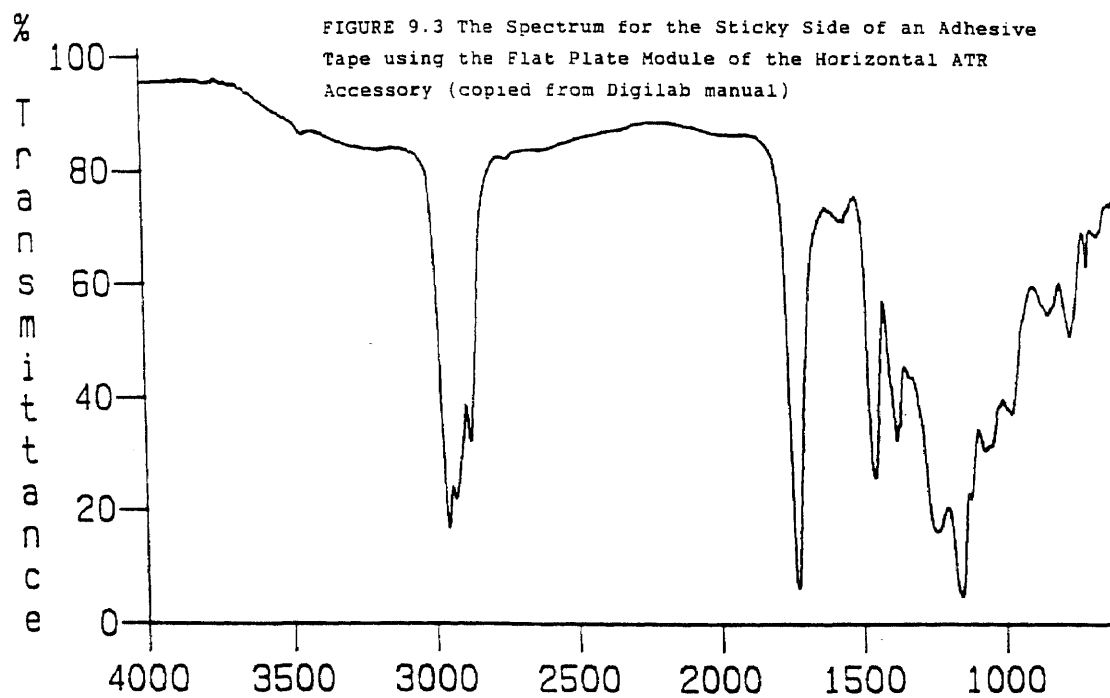
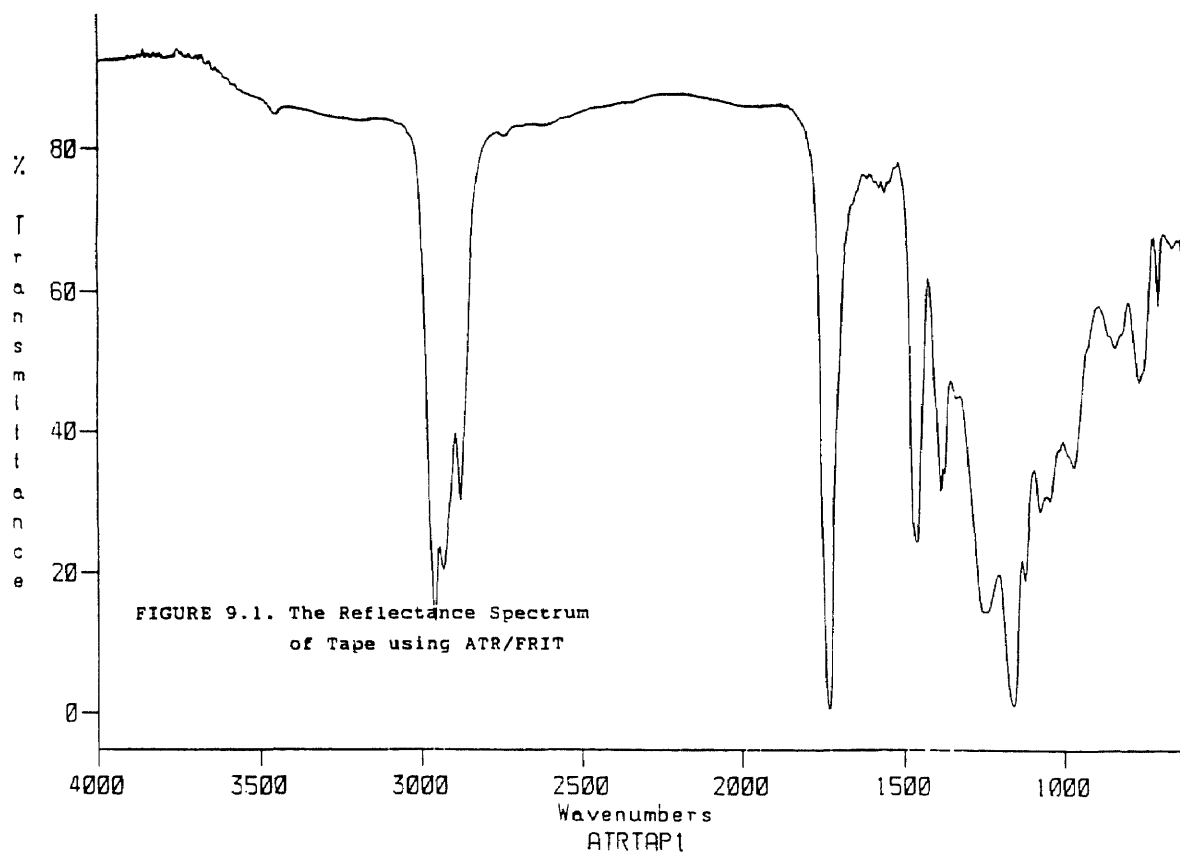
(1) The reflection spectrum of tape is shown in Figure 9.1.

(2) The reflection spectrum of kaolin is shown in Figure 9.2.

9.4 DISCUSSION

(1) Comparing Figure 9.1, reflection spectrum for the sticky side of an adhesive tape, with Figure 9.3, copied from the Bio-Rad manual, it is observed that they were similar. This means that the operations and parameters were used correctly in this study.

(2) Figure 9.2 is the spectrum of kaolin clay. Comparing it with Figure 9.4 copied from Sadtler Research Laboratories, it is seen that the major bands are almost same, which indicates that ATR/FTIR can be chosen for our study, for at least qualitative analysis. To get good spectra, the contact between the powder and the crystal is a very important factor. It may be helpful to use the pressure plate module of the Horizontal ATR accessory or to treat the powder sample using some special methods before scanning.



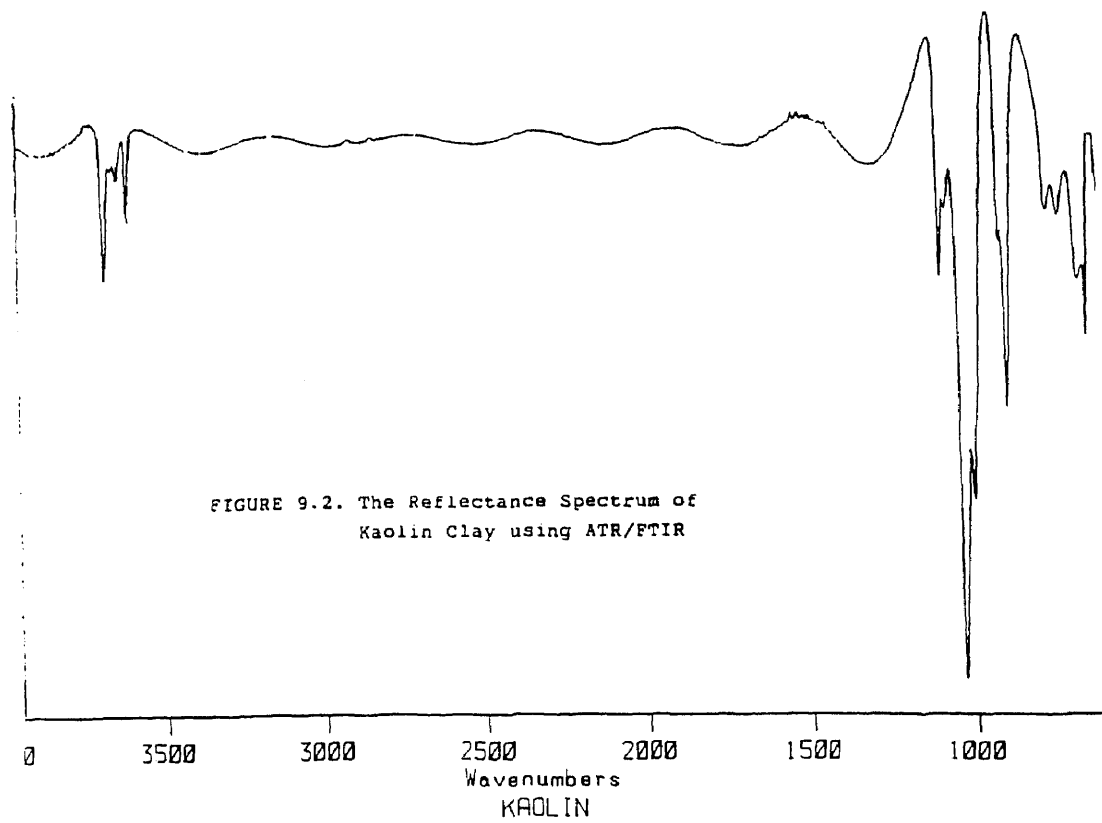
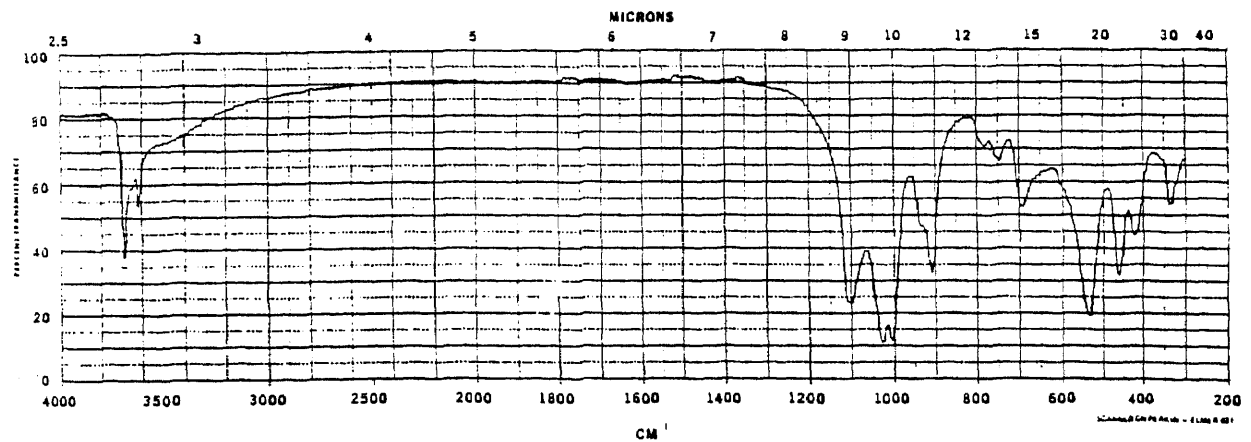


FIGURE 9.4 The Spectrum of Kaolin (copied from Sadtler Research Laboratories)



CHAPTER 10. EXPERIMENTAL SERIES VIII

THE INVESTIGATION OF SORPTION INTERACTIONS BETWEEN ANTHRAQUINONE AND HUMUS AFTER MICROWAVE TREATMENT USING DRIFT, GC/MS, AND GC/FTIR

10.1 INTRODUCTION

Recent scientific evidence indicates that natural soil functions as a dual sorbent for the uptake and release of nonionic organic compounds (Chiou and Shoup 1985; Chiou et al. 1988; Smith, Witkowski, and Chiou 1988). The mineral surfaces of the soil function as a conventional solid adsorbent and the soil organic matter functions as a partition medium.

During the decay process of organic materials, macromolecules of a mixed aliphatic and aromatic nature are formed. The term "humus" is widely accepted as synonymous with soil organic matter. It is defined as the total of the organic compounds in soil exclusive of undecayed plant and animal tissues, their partial decomposition products and the soil biomass. Some of the definitions of the various components of soil organic matter are presented in Table 10.1; average values of elemental composition (%) of humic substances from soil, lake sediment and various aquatic environments are listed in Table 10.2; and average values of major functional groups (carboxyl and phenolic hydroxyl) content of soil and aquatic humic substances are listed in Table 10.3 (Gerstl et al 1989).

TABLE 10.1.
DEFINITIONS OF VARIOUS COMPONENTS SOIL ORGANIC MATTER

Term	Definition
Organic residues	Undecayed plant and animal tissues and their partial decomposition products.
Soil biomass	Organic matter present as live microbial tissue.
Humus	Total of the organic compounds in soil exclusive of undecayed plant and animal tissues, their "partial decomposition" products, and the soil biomass.
Soil organic matter	Same as humus.
Humic substances	A series of relatively high-molecular-weight, brown to black colored substances formed by secondary synthesis reactions. The term is used as a generic name to describe the colored material or its fractions obtained on the basis of solubility characteristics. These materials are distinctive to the soil (or sediment) environment in that they are dissimilar to the biopolymers of microorganisms and higher plant (including lignin).
Nonhumic substances	Compounds belonging to known classes of biochemistry, such as amino acids, carbohydrates, fats waxes, resins, organic acids, etc. Humus probably contains most, if not all, of the biochemical compounds synthesized by living organisms.
Humin	The alkali insoluble fraction of soil organic matter humus.
Humic acid	The dark-colored organic material which can be extracted from soil by various reagents and which is insoluble in dilute acid.
Fulvic acid	The colored material which remains in solution after removal of humic acid by acidification.

TABLE 10.2
AVERAGE VALUES OF ELEMENTAL COMPOSITION (%)
OF HUMIC SUBSTANCES FROM SOIL, LAKE SEDIMENT
AND VARIOUS AQUATIC ENVIRONMENTS

Sample		C	H	O	N	P	S	Ash
Soil	FA	48.0	4.5	45.0	1.0	-	0.4	1.2
	HA	56.0	4.5	37.0	1.6	-	0.3	2.4
Lake sediment	FA	45.0	5.1	42.3	7.6	-	-	-
	HA	52.1	5.7	36.6	5.6	-	-	-
Lake water	FA	52.0	5.2	39.0	1.3	0.1	1.0	5.0
	HA	-	-	-	-	-	-	-
Ground water	FA	59.7	5.9	31.6	0.9	0.3	0.65	1.2
	HA	62.1	4.9	23.5	3.2	0.5	0.96	5.1
Seawater	FA	50.0	6.8	36.4	6.4	-	0.46	3.4
	HA	-	-	-	-	-	-	-
River water	FA	51.9	5.0	40.3	1.1	0.2	0.6	1.5
	HA	50.0	4.7	39.6	2.0	-	-	5.0
Wetland water	FA	51.0	4.3	40.2	0.7	0.2	0.4	2.0
	HA	51.2	4.4	40.9	0.6	0.1	0.6	2.0

TABLE 10.3
AVERAGE VALUES OF MAJOR FUNCTIONAL GROUPS
(CARBOXYL AND PHENOLIC HYDROXYL) CONTENT OF
SOIL AND AQUATIC HUMIC SUBSTANCES

Sample		Carboxyl (meq/g)	Phenolic (meq/g)
Soil	FA	5.2-11.2	0.3-5.7
	HA	1.5-5.7	2.1-5.7
Lake water	FA	5.5-6.2	0.3-0.5
Groundwater	FA	5.1-5.5	1.4-1.6
Seawater	FA	5.5	-
River water	FA	5.5-6.0	1.5
	HA	4.0-4.5	2.0
Wetland water	FA	5.0-5.5	2.5
	HA	4.0-4.5	2.5

Because of their polyelectrolytic nature, functional groups, and hydrophylic and hydrophobic sites, fulvic acid (FA) and humic acid (HA) fractions, humic substances are able to bind various organic compounds including pesticides, petrol, plastic derivatives, surfactants and detergents by various mechanisms which include physical and chemical adsorption, partitioning, solubilization, hydrolysis, photosensitization, and others (Stevenson 1972; Hayes and Swift 1978; Gerstl et al. 1989)

In the previous phase of this study, the investigation was focused on the mineral part of soil (clay). The results of that study showed that an insoluble, non-volatile

organic compound, namely, anthraquinone could be fixed on the clay after microwave energy treatment. IR spectra gave the direct evidence. This phase of the study was carried out on the interactions between anthraquinone and organic matters in the soil (humus) by DRIFT, GC/MS, and GC/FTIR.

10.2 EXPERIMENT

10.2.1 Instrumentation

For following spectroscopic changes in the humus before and after microwave treatment, a Digilab FTS-40 FTIR was used with a diffuse reflectance accessory to collect reflectance spectra of humus and anthraquinone-impregnated humus before and after microwave treatment. Conditions are: 8 cm^{-1} resolution, 68 scans, and DTGS detector.

For the analysis of extracts from the humus, GC/MS was used in the same way as in the previous study. Also, GC/FTIR was used.

A Digilab FTS-40 FTIR spectrophotometer and a Hewlett-Packard model 5890A gas chromatograph equipped with a flame ionization detector were used in this study. The spectrometer was equipped with a Digilab GC/C-32 accessory, which includes a gold coated, heated light-pipe, and contains its own high sensitivity, liquid-nitrogen-cooled, mercury-cadmium-telluride detector. Infrared data collection and manipulation were performed using Digilab GC-32 software. 4 scans at 8 cm^{-1} resolution were co-added for each scan set, giving a time resolution of approximately one second. A PONA capillary column (12 m x 0.22 mm, 0.5 μm thickness) was used for obtaining the chromatographic separation. In

a GC/FTIR run, a gas chromatograph separates a complex, volatile mixture, and the resulting vapor phase eluents flow through a specially-designed, high temperature infrared gas cell, commonly called a light-pipe. The beam from an FTIR spectrometer is passed through this lightpipe, and is then directed onto a sensitive detector. Interferograms are collected continuously, with a set of four, requiring about one second total acquisition time, being co-added to form a scan-set. These scan-set can be stored for later manipulation. A 0.1 microliter aliquot of the extract from the humus sample was injected and separated under the following chromatographic conditions:

Light pipe temperature: 270 °C

Transfer temperature: 270 °C

Injection port temperature: 220 °C

Detector temperature: 300 °C

Initial oven temperature: 50 °C

Final oven temperature: 250 °C

Temperature increase rate: 6 °C/min

10.2.2 Materials

Humus used in this study was taken from. All other materials used were as same as those in the previous studies.

10.2.3 Experimental procedure

Step 1. Humus soil was put in an air conditioned room for five days, crushed, and sieved to less than 38 μ m diameter.

Step 2. Fifty gram humus soil was used as the background. The reflectance spectra of the samples were collected by DRIFT before and after microwave treatment.. The extracts from the humus soil were analyzed by GC/MS and GC/FTIR.

Step 3. Fifty milliliter of anthraquinone solution was transferred to fifty gram humus soil. The anthraquinone-impregnated humus soil was put in a hood for 2 days to evaporate solvent and then treated by microwave energy. The reflectance spectra of the samples were collected by DRIFT before and after microwave treatment. The microwave treatment time was chosen 7 minutes. The extracts were detected by GC/MS and GC/FTIR.

10.3 EXPERIMENTAL RESULTS

A reflectance spectra of humus, before and after microwave treatment, are shown in Figure 10.1a and Figure 10.1b.

A reflectance spectrum of anthraquinone-impregnated humus soil before microwave treatment is presented in Figure 10.2a.

A reflectance spectrum of anthraquinone-impregnated humus soil treated by microwave energy 7 minutes is given in Figure 10.2b.

The concentrations of anthraquinone in the extracts from the samples are presented in the Table 10.4 (detected by GC/MS).

10.4 Discussion and Conclusions

(1) Fourier transform infrared spectroscopy offers a number of advantages over conventional dispersive instruments for the characterization of humus like materials because of its higher resolution power. One important benefit of FTIR is that good spectra can be obtained from highly absorbing species. The reflectance spectrum of humus is shown in Figure 10.1a. This is compared to the spectra in Figure 10.3 (Painter and Coleman 1980). In Figure 10.3, the infrared spectra of an identical KBR pellet of humic acid on a conventional dispersive instrument and the Digilab FTS 15/B are compared. From Figure 10.3, it is evident that the FTIR spectrum is noticeably superior with respect to resolving bands. The general superiority of FTIR spectra is a consequence of the optical advantages inherent in using an interferometer rather than a system of gratings and slits. Comparing the reflectance spectrum and Figure 10.3, it is also seen that DRIFT can be used to obtain a good spectrum from highly absorbing species.

(2) From the Table 10.4, it is observed that the concentration of anthraquinone decreased sharply after microwave energy treatment. This result also indicates that microwave technology can be used to remediate humus soil contaminated with non-volatile organics.

TABLE 10.4
THE CONCENTRATION OF ANTHRAQUINONE
IN THE EXTRACT FROM HUMUS SOIL

Name	Concentration	C/Co	Temperature Treating time
AHU1	176.8 ppm	1 (blank)	
AHUH1	56.05 ppm	0.32	7 min

(3) Comparing the reflectance spectra of anthraquinone-impregnated humus soil before and after microwave treatment, unlike the previously-discussed kaolin study, the carbonyl band of anthraquinone cannot be used to follow the interaction between anthraquinone and humus because there is also a carbonyl band in the humus. However, other absorption bands were available to follow in this study. It is seen that band shifts occurred, and that some new bands were formed, especially, in region of 2222 cm^{-1} . No change could be observed in this region when humus was alone treated by microwave energy (see Figure 10.1b). This observation indicates that microwave energy can cause an interaction between anthraquinone and humus. That absorption band can be ascribed to changes in the cumulative double bond structures due to the interaction of anthraquinone with soil causing the anthraquinone no longer to be symmetrical: changes in cumulative double bonds appear in this region of the infrared spectrum. Of course, it is recognized that this is a highly tenuous assignment. The specific structural source of that band and other band changes will be the focus of future studies.

(4) The study of GC/FTIR also shows that the concentration of anthraquinone in the extract from the humus decreased after microwave treatment. The use of GC/FTIR as an applied analytical technique has been shown for drinking water (Azarrage 1975), industrial wastewater (Azarraga and McCall 1974, Keith 1975, Keith 1976), water from in situ coal gasification plants (Erickson et al. 1977, Erickson and Pellizzari 1977), pyrolysis products (Clark et al. 1978), pesticides (Wall and Mantz 1978), biochemical samples (Mantz 1977), and commercial samples (Sadtler research lab.). A review of these applications appears in a recent publication by Erickson (Erickson). With the advent of GC/FTIR analysis of real samples comes the opportunity to supplement GC/MS analysis. The combination of these two techniques can provide absolute identification of a component where each individual technique only presented a choice of possible identifications (Shafer et al. 1979). Usually, GC/MS can often provide information leading to an empirical formula, but this information is insufficient in content to enable precise structural formula identification, whereas GC/FTIR, by its capability to identify substitution patterns of molecules, affords a means of precise determination of the structural formula. Therefore, for the future study, the application of the combined analytical techniques of GC/FTIR and GC/MS may be useful to the analysis of unknown compounds.

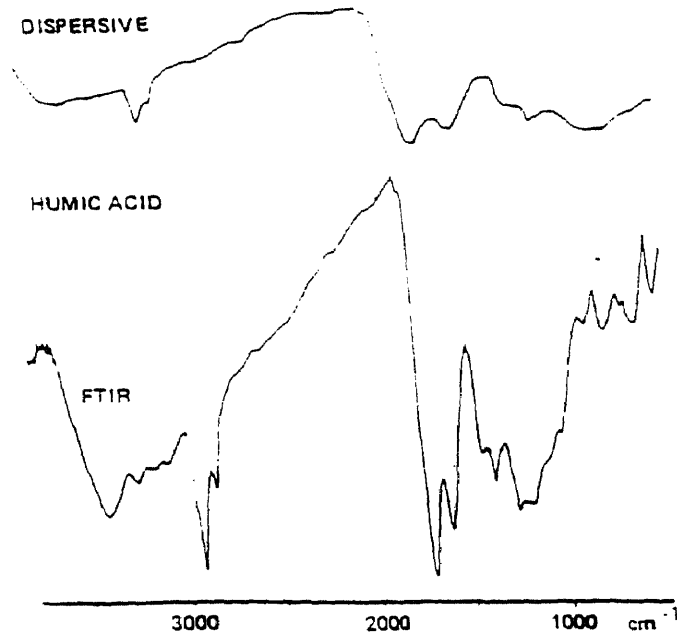
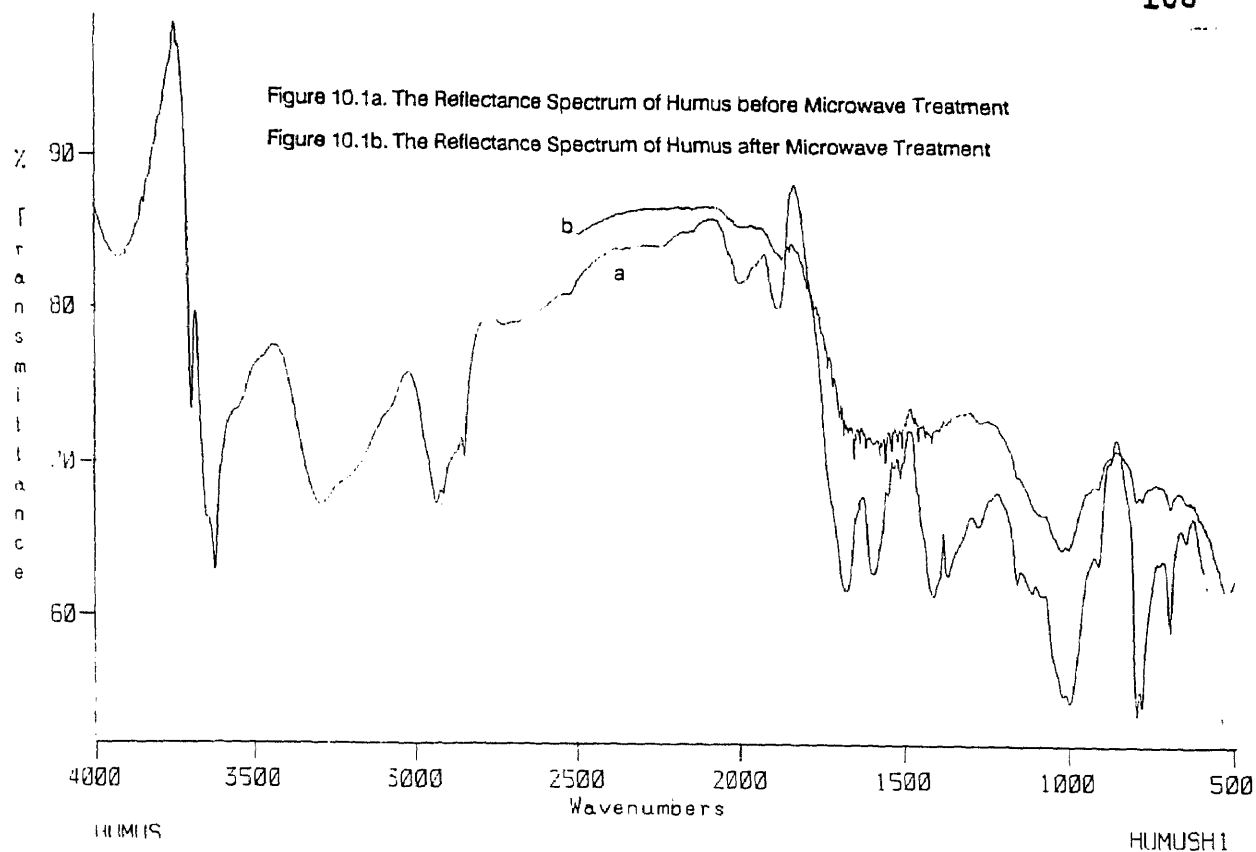
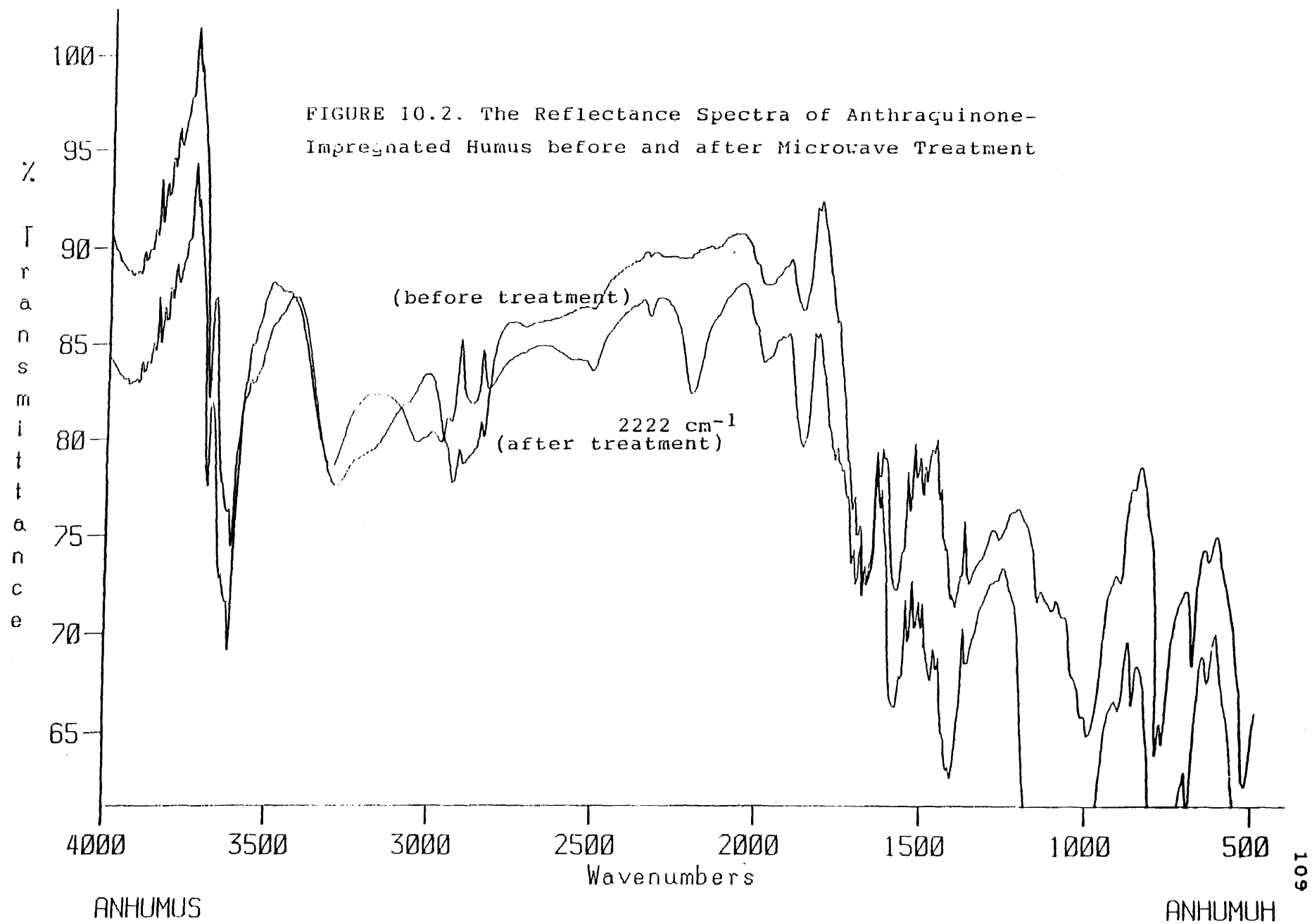


Figure 0.3 A comparison of the infrared spectra of an identical KBr pellet of Humic Acid recorded on a conventional dispersive instrument and the Digilab FTS 15/B.



CHAPTER 11. CONCLUSIONS AND FUTURE RESEARCH NEEDS

Microwave treatment of hazardous wastes like dioxin-contaminated soil potentially fills a great need for a remediation technology which can be applied in-situ. The Environmental Protection Agency (USEPA) has concluded from a risk assessment study that the greatest risks to the environment and human health will arise from the excavation of a site and the transportation of the dioxin-contaminated soil to a treatment facility. (Moreover, no treatment facility of any type, for the dioxin-contaminated soil, is now available in the United States.)

In-situ treatment is possible because microwave treatment is effected by the propagation of electromagnetic radiation waves of relatively long wavelengths. Such waves can be transferred by propagation through air from an antenna in the power source and be received by an antenna buried in the ground.

Studies have been carried out in several stages on a surrogate for dioxin, namely, 9,10-anthraquinone, because it has similar chemical and physical properties but it is not toxic. In the initial study it was found that microwave treatment, at relatively low temperatures which are potentially attainable in-situ, rendered the anthraquinone in the soil non-extractable. This investigation was carried out on both anthraquinone-impregnated sandy soil and clay soil, respectively. Extracts were analyzed by GC/MS and FTIR, respectively. The studies showed that, during microwave energy treatment, chemical fixation possibly occurred sharply at the relatively low temperature of 200 °C. Little anthraquinone could be detected in the extracts from the clay soil above 300 °C.

The results of this study also indicate that water might play an important role during the microwave treatment. Adding water before microwave treatment may speed up the reduction of the concentration of anthraquinone in the extract.

In addition, the study showed that the extractability of anthraquinone in the soil was affected by water. By adding water, the extractability increased 14% for sandy soil and 13% for clay soil. This indicates that sorption of non-volatile and non-polar compounds decreases as soil moisture content increases. The natural soil functions as a sorbent for uptake and release of nonionic organic compounds. In the absence of water (polar molecules), nonionic compounds will occupy more binding sites of soil. By contrast, in an aqueous system, a much stronger competitive adsorption of water on the soil surface will result in suppression of sorption of organic compound.

From those studies, the following model was proposed: soil particles are bound together by water internally and externally; a spilled organic like dioxin forms multilayers on the soil particles in which the multilayers are held together by relatively weak Van der Waal's forces because water can not be displaced; microwave treatment directly volatilizes the water, because water is by far the strongest microwave absorber present, creating sites for unimolecular adsorption of the organic on the soil, further heating of the soil causes the organic to react chemically, and thus chemical fixation is effected.

The validity of this model depends upon whether or not, in fact, "chemical fixation" has occurred. This led to spectroscopic studies which had the potential to provide chemical information about interactions between the organic and humus and clay, respectively. The spectroscopic methods tried were DRIFT (diffuse reflectance

Fourier transform infrared spectroscopy) and attenuated total reflectance spectroscopy (ATR). In both of these methods it is the surface of the solid which acts as the absorber of infrared radiation. The major difference is the nature of the reflected radiation: in DRIFT, it is diffuse reflection; in ATR, internal reflection.

Studies were carried out on both anthraquinone-impregnated humus soil and kaolin clay, respectively, using diffuse reflectance Fourier transform spectroscopy (DRIFT), GC/FTIR, and attenuated total reflectance Fourier transform spectroscopy (ATR/FTIR).

In the kaolin clay studies, it was found that no changes in the absorption bands occurred when the kaolin clay was impregnated with anthraquinone. Furthermore, it did not appear that the kaolin clay absorbed microwave energy and heated up. Therefore, a susceptor was added, that is, a material which is strong absorber, specifically, the mineral magnetite. Afterwards, band shifts were observed after microwave treatment. It has been concluded in a monograph on the subject of clay-organic interactions that kaolin, because of its tight two layer structure, will not absorb large non-polar molecules. Thus, in this study, the observance of a band shift for a system consisting of kaolin and a large non-polar molecule like anthraquinone is of general significance. The band shift observed was in the region of the carbonyl stretching frequency. The appearance of a shoulder band indicates that the symmetry of the molecule has changed, therefore, the two carbonyl groups are no longer in the same environment, and will have different stretching frequencies. Future studies will focus on further defining the nature of this interaction.

Turning next to the results from the study of anthraquinone on humus, this system absorbed microwave energy so that there was no need for the addition of a susceptor. Band shifts, and band appearances and disappearances were observed. Changes in the carbonyl stretching frequencies could not be observed because humus alone strongly absorbs in this region. However there were changes in the cumulative double bond absorption region. These changes could be ascribed to interactions with the humus bringing about asymmetry in the aromatic molecules. Again this is a tentative conclusion necessitating further study.

It is not the assignments for the band shifts which are of major significance but that the with the techniques employed such shifts could be observed, thus, opening up for investigation a critical area of theoretical and practical importance: a) the theoretical importance is that molecular models of organic-soil interactions to-date have been based upon the indirect data obtained from extraction/adsorption studies; in this study direct data is obtained and more accurate useful models can be formulated; b) the practical importance is that because the question of whether or not a soil remediation technology will be effective over a long period of time ultimately depends upon the chemical and physical fate of the organic in the soil.

(Future Work)

The results of this study raise the following questions: Will heat alone be effective or is the microwave heating of the magnetite critical? Will higher temperatures strengthen the adsorption or chemical changes? What is the origin of the band shifts and formation observed. Besides, although the boiling point of anthraquinone is 380 °C, it has a significant vapor pressure at low temperature.

Evaporation is enhanced by the presence of water, since steam distillation will allow anthraquinone to be evaporated at a lower temperature. Therefore, more detailed work on the vapor phase is needed. Future study must be carried out concerning all those questions.

APPENDIX I. OPERATING PARAMETERS

ACQUISITION PARAMETER FILE (GC/MS)

DATA:ZH-FILE.A

Miscellaneous

Description : STANDARD
 Operator : NINA
 Date & time : 21 Feb 91 3:57 pm
 Inlet : GC
 Configuration file : DATA:TCETUNE.U
 Acquisition mode : Scan
 Electron Multiplier : -200.00
 EM absolute : FALSE

Temperature Zones

Initial temperature : 80.00
 Initial time : 0.00
 Equilibration time : 0.20

	Set Points	Soft Limits	Status
Oven	80	300	On
Inj Port A	0	250	Off
Inj Port B	185	250	On
Transfer Line	280	300	On
Ion Source	0	250	On
Mass Analyzer	0	300	On
Detector A	0	250	Off
Detector B	0	0	On

*** Integrator Events ***

Initial Peak Width 0.100
 Initial Threshold 4
 Initial Area Reject 1
 Shoulders OFF

9.001 Integ ON
 9.001 Area Sum ON
 10.997 Integ OFF
 10.997 Area Sum OFF

DRIFT and ATR/FTIR Operating Parameters

```

((( parameter set CURRENT.PV )))
APT=OPEN          LEFT=3500.0      SAMP10=          UDR=2
APTY=TRIANG       MENCOL=740b80b00b00SAMP2=AKK1T      XSB=0
BACK=KBR2        MICRONRES=0.01    SAMP3=          XSCALE=100
BANDEDGE1=0.2     MORE=N           SAMP4=          XSIZE=AUTO
BANDEDGE2=0.8     NEWSPEC=AB1T      SAMP5=          YMAX=AUTO
BEAM=INT          NLV=0.05          SAMP6=          YMIN=AUTO
DAPTY=TRIANG      NPOINTS=AUTO      SAMP7=          YSCALE=100
DELAY=1.0         ORDER=2           SAMP8=          YSIZE=AUTO
DET=INT           ORIENT=NORMAL      SAMP9=          ZFF=2
DSPCOLOR=DIFFERENT PAPERSIZ=SM      SCANS=64
DSPMOVE=TOGETHER  PAXES=Y           SCANTO=TR
DSPOFFSET=NONE    PCOMM=NONE        SCBACK=1.000
ELWN=15800.8235   PEN=AUTO          SCNSTD=256
ENP=AUTO          PKSENS=1          SCSAMP=1.000
FFP=4000.0        PKSOURCE=G/S      SEN=4
FGNULL=/usr/lib/fgnPKTAB=Y          SIGNAL=AUTO
FGREG=/usr/lib/fgrePLABEL=ATC 313 LAB. SPEC=SPEC40
FILTLO=1          PLOTPAGE=Y         SPEED=5
FLP=400.0         PLOTTER=AUTO       SSP=NO
FLTRTP=BP         PLUNITS=CM         STP=AUTO
GCAP=N            PPARMS=RES         SUBFAC=0.0
GCDELAY=0         PSDESC=           SUBTYPE=H2O
GCNBACK=20        PXOFF=0.0         SUMAX=AUTO
GCNBASIS=20       PYOFF=0.0         SUMIN=AUTO
GCTIME=45         REF=POLYR          SVIG=N
GRR=40            RES=4             SVIM=N
HWIDTH=10.0       RIGHT=3300.0       SVMR=N
INTFACT=1         RUNCOMMENT=        SVSB=N
KMBASE=AUTO       RUNTITLE=         SYM=ASYM
KVAL=2.0          SAMP=AB1T          TRANSBW=0.05

```

APPENDIX II. EXPERIMENTAL RAW DATA

AN-BLW1

Peak Num	Type	Int Type	Ret Time	Signal Description	Compound Name	Area	Amount
1		1BH +	9.326	207.00- 210.00 amu		5895255	842.5 ng/ul

AN-TU1

Peak Num	Type	Int Type	Ret Time	Signal Description	Compound Name	Area	Amount
1		1BH +	9.288	207.00- 210.00 amu		4024089	589.1 ng/ul

AN-TU2

Peak Num	Type	Int Type	Ret Time	Signal Description	Compound Name	Area	Amount
1		1BH +	9.273	207.00- 210.00 amu		1646197	267.1 ng/ul

AN-TU3

Peak Num	Type	Int Type	Ret Time	Signal Description	Compound Name	Area	Amount
1		1BH +	9.250	207.00- 210.00 amu		1612306	262.5 ng/ul

AN-BLS1

Peak Num	Type	Int Type	Ret Time	Signal Description	Compound Name	Area	Amount
1		1BH +	9.376	207.00- 210.00 amu		6665097	946.8 ng/ul

AN-TS1

Peak Num	Type	Int Type	Ret Time	Signal Description	Compound Name	Area	Amount
1		1BH +	9.325	207.00- 210.00 amu		5837483	834.7 ng/ul

AN-TS2

Peak Num	Type	Int Type	Ret Time	Signal Description	Compound Name	Area	Amount
1		1BH +	9.251	207.00- 210.00 amu		2536921	387.8 ng/ul

	Peak Num	Type	Int Type	Ret Time	Signal Description	Compound Name	Area	Amount
ANSL2R	1		188 +	9.546	207.00- 210.00 amu		15433031	2134 ng/ul

	Peak Num	Type	Int Type	Ret Time	Signal Description	Compound Name	Area	Amount
ANSL2	1		188 +	9.570	207.00- 210.00 amu		13753043	1807 ng/ul

	Peak Num	Type	Int Type	Ret Time	Signal Description	Compound Name	Area	Amount
AN2BLU1	1		18H +	9.354	207.00- 210.00 amu		6657881	945.8 ng/ul

	Peak Num	Type	Int Type	Ret Time	Signal Description	Compound Name	Area	Amount
AN2BLU1R	1		18H +	9.304	207.00- 210.00 amu		6700103	951.5 ng/ul

	Peak Num	Type	Int Type	Ret Time	Signal Description	Compound Name	Area	Amount
AN2BLU2	1		18H +	9.290	207.00- 210.00 amu		6077084	867.1 ng/ul

	Peak Num	Type	Int Type	Ret Time	Signal Description	Compound Name	Area	Amount
AN2BLU2R	1		18H +	9.178	207.00- 210.00 amu		7106245	1006 ng/ul

	Peak Num	Type	Int Type	Ret Time	Signal Description	Compound Name	Area	Amount
AN2BLS1	1		18H +	9.270	207.00- 210.00 amu		7433675	1051 ng/ul

	Peak Num	Type	Int Type	Ret Time	Signal Description	Compound Name	Area	Amount
AN3BLU1	1		18H +	9.320	207.00- 210.00 amu		8103834	1142 ng/ul

	Peak Num	Type	Int Type	Ret Time	Signal Description	Compound Name	Area	Amount
AN3BLU1R	1		18H +	9.341	207.00- 210.00 amu		7728813	1091 ng/ul

	Peak Num	Type	Int Type	Ret Time	Signal Description	Compound Name	Area	Amount
AN3BLU2R	1		18H +	9.285	207.00- 210.00 amu		8640906	1214 ng/ul

	Peak Num	Type	Int Type	Ret Time	Signal Description	Compound Name	Area	Amount
AN3BLS1	1		18H +	9.179	207.00- 210.00 amu		8306913	1169 ng/ul

	Peak Num	Type	Int Type	Ret Time	Signal Description	Compound Name	Area	Amount
AN3BLS2	1		18H +	9.361	207.00- 210.00 amu		8787633	1234 ng/ul

ANSL3	Peak	Int	Ret	Signal	Compound	Area	Amount
	Num Type Type	Time	Description	Name			
	1	188 +	9.581	207.00- 210.00 amu		21865047	2978 ng/ul
ANSL3R	Peak	Int	Ret	Signal	Compound	Area	Amount
	Num Type Type	Time	Description	Name			
	1	188 +	9.580	207.00- 210.00 amu		21444730	2948 ng/ul
AN4BL1R	Peak	Int	Ret	Signal	Compound	Area	Amount
	Num Type Type	Time	Description	Name			
	1	18H +	9.256	207.00- 210.00 amu		6462422	919.3 ng/ul
AN4BL12	Peak	Int	Ret	Signal	Compound	Area	Amount
	Num Type Type	Time	Description	Name			
	1	18H +	9.303	207.00- 210.00 amu		7055452	999.6 ng/ul
AN5BL11	Peak	Int	Ret	Signal	Compound	Area	Amount
	Num Type Type	Time	Description	Name			
	1	188 +	9.250	207.00- 210.00 amu		9099543	1276 ng/ul
AN5BL12	Peak	Int	Ret	Signal	Compound	Area	Amount
	Num Type Type	Time	Description	Name			
	1	18H +	9.293	207.00- 210.00 amu		8416657	1184 ng/ul
AN5BL1R	Peak	Int	Ret	Signal	Compound	Area	Amount
	Num Type Type	Time	Description	Name			
	1	18H +	9.119	207.00- 210.00 amu		8692903	1221 ng/ul
AN5BL2	Peak	Int	Ret	Signal	Compound	Area	Amount
	Num Type Type	Time	Description	Name			
	1	18H +	9.227	207.00- 210.00 amu		9661492	1353 ng/ul

/ANTR2	Peak	Int	Ret	Signal	Compound	Area	Amount
	Num Type Type	Time	Description	Name			
	1	1BH +	9.147	207.00- 210.00 amu		888899	164.6 ng/ul
/ANTR2R	Peak	Int	Ret	Signal	Compound	Area	Amount
	Num Type Type	Time	Description	Name			
	1	1BH +	9.168	207.00- 210.00 amu		957057	173.8 ng/ul
/ANTR4	Peak	Int	Ret	Signal	Compound	Area	Amount
	Num Type Type	Time	Description	Name			
	1	1BH +	9.157	207.00- 210.00 amu		118308	60.24 ng/ul
/ANTR6R	Peak	Int	Ret	Signal	Compound	Area	Amount
	Num Type Type	Time	Description	Name			
	1	1BH +	9.141	207.00- 210.00 amu		272378	81.11 ng/ul
/ANTR6	Peak	Int	Ret	Signal	Compound	Area	Amount
	Num Type Type	Time	Description	Name			
	1	1BH +	9.152	207.00- 210.00 amu		317098	87.15 ng/ul
/ANTR8?	Peak	Int	Ret	Signal	Compound	Area	Amount
	Num Type Type	Time	Description	Name			
	1	1	-----	207.00- 210.00 amu		*** Not Found ***	
/ANTR10	Peak	Int	Ret	Signal	Compound	Area	Amount
	Num Type Type	Time	Description	Name			
	1	1BH +	9.046	207.00- 210.00 amu		7748	45.27 ng/ul
/ANTR12	Peak	Int	Ret	Signal	Compound	Area	Amount
	Num Type Type	Time	Description	Name			
	1	1	-----	207.00- 210.00 amu		*** Not Found ***	
AHU1	Peak	Int	Ret	Signal	Compound	Area	Amount
	Num Type Type	Time	Description	Name			
	1	1BH +	9.139	207.00- 210.00 amu		979427	175.8 ng/ul
AHUHI	Peak	Int	Ret	Signal	Compound	Area	Amount
	Num Type Type	Time	Description	Name			
	1	1BH +	9.131	207.00- 210.00 amu		87362	56.05 ng/ul

APPENDIX III.

Publications/Presentations/Theses
from
Microwave Treatment of Hazardous Wastes Laboratory
of the
Hazardous Substance Management Research Center

Director: Dr. Leonard Dauerman

Co-Director Gabriele Windgasse

Dauerman, L. and Windgasse, G., "Microwave Treatment of Hazardous Wastes", TIZ International (German-English), Vol. 114- NO. 7/8, pp 503-506, 1990.

Dauerman, L. and Windgasse, G., "Microwave Treatment of Hazardous Wastes", Mikrowellen & HF Magazin, Vol. 16, No. 4, pp 329-331, 1990.

Dauerman, L. and Windgasse, G., Microwave Treatment of Hazardous Wastes: Chemical Mechanisms, Industrial Microwave Processing Conference, Deakin University, Geelong, Australia, July 12, 1990.

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